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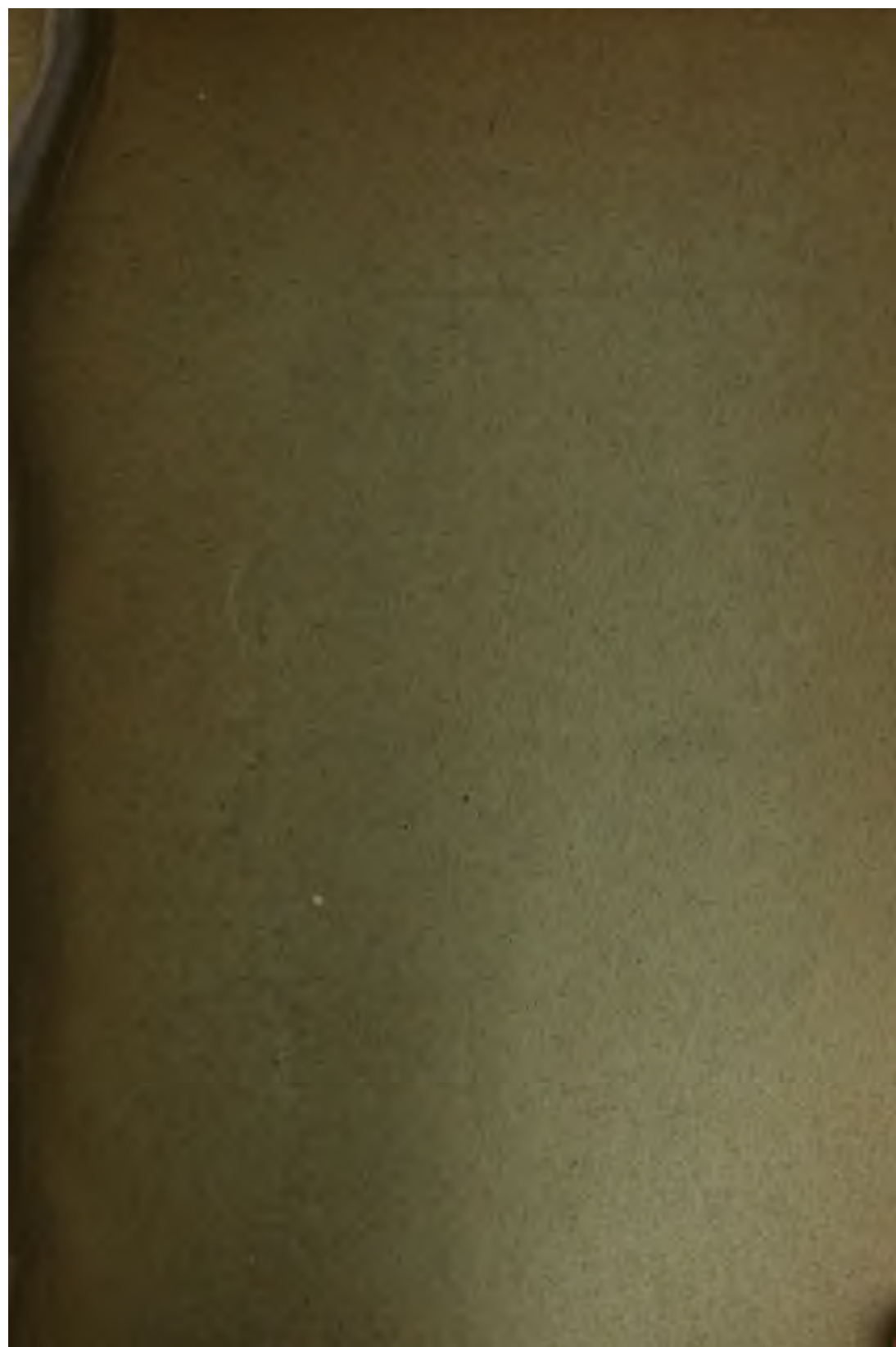


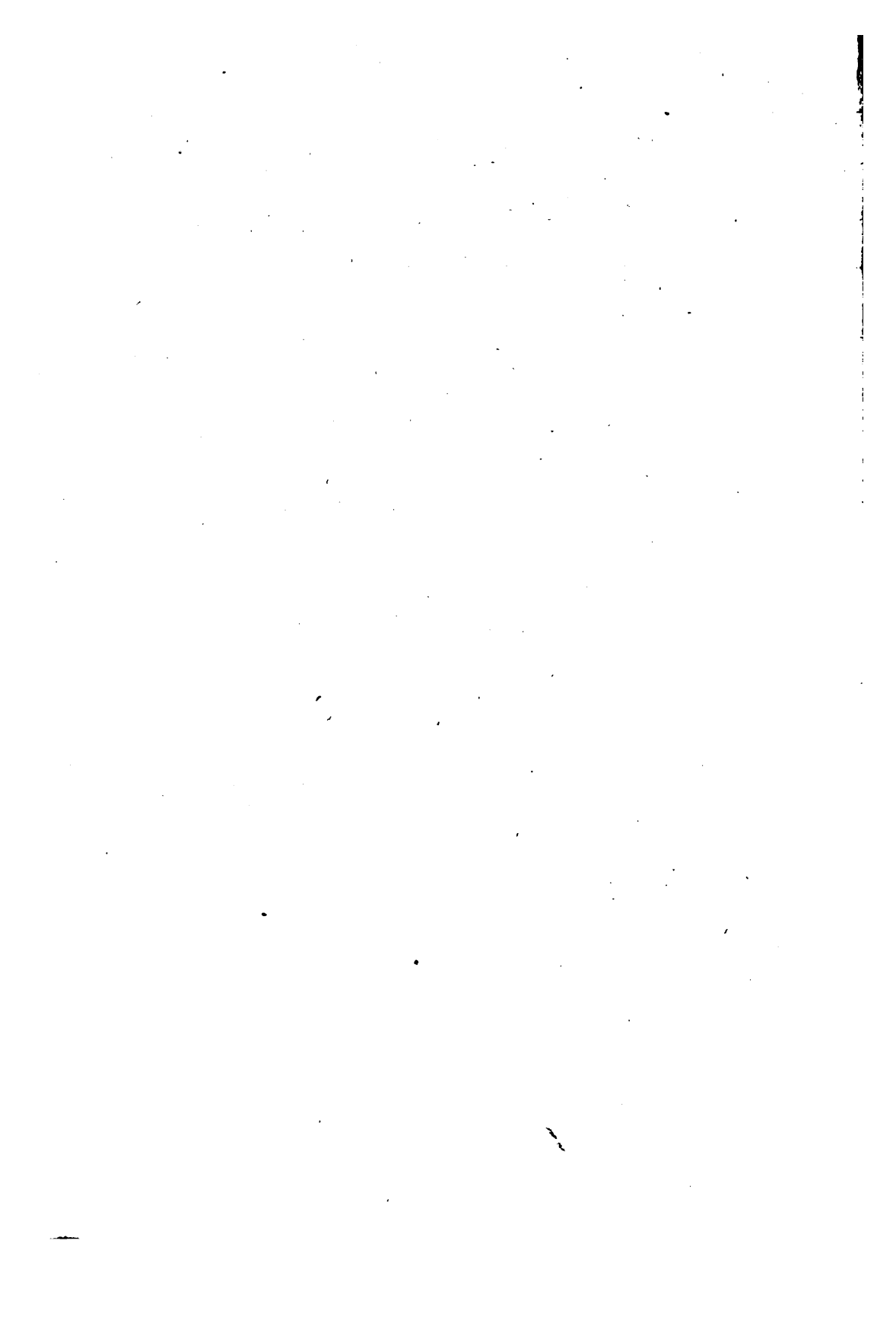
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THE JOURNAL

OF THE

American Chemical Society

VOL. XXXVII

JULY—DECEMBER

1915



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THE JOURNAL
OF THE
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CONCERNING THE COMPRESSIBILITIES OF THE ELEMENTS,
AND THEIR RELATIONS TO OTHER PROPERTIES.

By T. W. RICHARDS.

Received May 8, 1915.

In an extended paper published eight years ago, a number of experiments were described, having for their aim the determination of the compressibilities of thirty-five elements.¹ The object was to determine especially the periodicity of the compressibilities in relation to the atomic weight and to other properties of these fundamental substances. All the values were referred to that of mercury, although it was explicitly recognized at that time that the value for mercury was somewhat in doubt.² This was done, because such an error, if present, must affect each value equally:—the doubt could not invalidate the main point of the work; therefore, instead of spending much time, labor and money upon the determination of the absolute compressibility of mercury, the experimenters studied the various other elements. When the compressibility of mercury became more accurately known, the results could all be easily corrected to the better standard without additional experimental work.

¹ Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst. Wash.*, No. 76 (1907).

² *Ibid.*, on page 64 the following statement was made: "In comparing these results it must be borne in mind that all depend upon the still somewhat uncertain compressibility of mercury"

This time now seems to have come. The recent work of Bridgman at high pressures and that of the author in conjunction with E. P. Bartlett,¹ and yet more recently with J. H. Hodges,² at lower pressures have put this quantity in the list of those very accurately determined; accordingly, it is appropriate that the older results should be corrected to the true standard.

Moreover, a better standard of pressure is now available. The two Bourdon pressure gages used in 1903-1907 were not perfect, and could be relied upon only for relative results, as was fully recognized at the time.³ Fortunately, since this earlier work was finished, two new independent and entirely satisfactory absolute pressure gages have been at our disposal, and the old Bourdon gages have been compared with them, so that in this respect also the older results may be corrected and put upon a more permanent footing.

A study of the relation between each of the old gages and Bridgman's absolute standard is given in a diagram in an earlier paper.⁴ The Bridgman gage, when connected with our extremely accurate gage, gives essentially identical results,⁵ so that one may feel confident of the joint indication. From the mean of several comparisons of the old Bourdon gages with the new absolute standard, the following table of corrections to be applied to the average between the two old gages has been compiled:

CORRECTIONS TO AVERAGE OF BOURDON GAGE.

Reading.	Cor.	Reading.	Cor.	Reading.	Cor.
50	+0.5	250	+1.0	450	+2.0
100	0.0	300	0.5	500	+2.0
150	+1.0	350	+2.0	550	0.0
200	+1.0	400	+2.0

This table, which agrees essentially with the diagram already mentioned, is made out, for convenience, upon the assumption that the 100-atmosphere point was without error, as this was always the starting point. No effort was made to record the values more nearly than to within 0.5 atmosphere, because the early work was not carried beyond this degree of refinement. These values, then, are the corrections to be applied to the recorded pressures of 1907 in order to bring them to the true standard. Evidently the error between 100 and 500 is only about one-half of one per cent. of the interval, so that the figures are but little altered by the correction. Accordingly, the new values for the compressibilities differ from the old ones (given in the early publication) in most cases

¹ Richards and Bartlett, *THIS JOURNAL*, 37, 470 (1915).

² As yet unpublished.

³ *Pub. Carnegie Inst. Wash.*, No. 76, 14 (1907).

⁴ *THIS JOURNAL*, 34, 793 (1912).

⁵ Richards and Shipley; investigation as yet unpublished.

only by the addition to each compressibility of the quantity 0.00000016—the error of the formerly assumed value of the compressibility (0.00000379) of the standard substance, mercury (now taken as 0.00000395).¹ In the cases of iron, copper, lead and molybdenum, the new values, determined more accurately with the help of E. P. Bartlett,² have been substituted for the old ones, which after correction were not very different, but which were doubtless less trustworthy. The new results of the same investigation giving data for tungsten and tantalum have also been included in the table, and so has a preliminary value determined here with the help of J. H. Hodges for boron, this substance having been kindly furnished in a very pure state by Dr. Weintraub of the works of the General Electric Company, at Lynn, Mass. This last research has not yet been published.

The table below contains the recalculated record of the compressibility of 38 elements, of which 35 are solid under the conditions of measurement and 3 liquid. These values are all expressed as $\frac{(\Delta v)_{100-500}}{v_0 \Delta p}$, that is, in terms of the average fractional change of volume caused by 1 megabar's pressure between 100 and 500 megabars, referred to the volume of the uncompressed substance. The values, as has been said, are all determined at 20° by reference to mercury, the compressibility of which is recorded below. If this last named value should be found to demand a slight further correction at some future date, the same actual correction will apply additively to each figure given.

The megabar (or megabarie) is chosen as the measure of pressure, because this logical absolute unit, having received international recommendation, bids fair to become the scientific standard of the future. Being the pressure of one megadyne per square centimeter, it is almost 2% greater than the kilogram per square centimeter, and 1.3% less than the "atmosphere." In many of the present cases the difference between these standards does not exceed greatly the experimental limit of error. The values may be easily transposed into terms of the atmosphere by adding in each case 1.3%.

In addition to the compressibilities of these several elements, the table records also in subsequent columns the atomic volumes, densities, melting points recorded in absolute temperature, coefficients of expansion and, finally, international atomic weights, since the compressibilities will

¹ Credit should be given to Grüneisen for pointing out that an error of about 0.0000002 probably existed in the earlier published results, although he was not able to guess the cause of the error. The reason for taking mercury as 0.00000395 instead of 0.00000396 as found by Richards and Bartlett will be explained in a coming paper by one of us in conjunction with J. H. Hodges. (See Grüneisen, *Ann. der Physik.*, [4] 25, 849 (1908); also footnote, *ibid.*, [4] 26, 397 (1908).)

² *Loc. cit.*

COMPRESSIBILITIES, ATOMIC VOLUMES, DENSITIES, MELTING POINTS, COEFFICIENTS
OF EXPANSION AND ATOMIC WEIGHTS OF A MAJORITY OF THE COMMONLY
SOLID AND LIQUID ELEMENTS AT 20° C. BETWEEN 100 AND
500 MEGABARS (IF THE COMPRESSIBILITY OF
MERCURY = 0.0000395).

	Average compressibility at 20° (see above) $\times 10^6$.	Atomic volume.	Density at 20°.	Melting point (absolute temp.).	Cubic coefficient of expansion $\times 100,000$.	International atomic weight (1914).
Lithium.....	9.0	13.1	0.534	453	19.	6.94
Boron.....	0.3	4.7	2.34	2800 ¹	...	11.0
Carbon, diamond...	Very small	3.4	3.51	Very high	0.3	12.00
Carbon, graphite....	3.0	5.4	2.26	Very high	7.2	12.00
Sodium.....	15.6	23.7	0.971	371	22.0	23.00
Magnesium.....	2.9	13.3	1.74	927	7.8	24.32
Aluminium.....	1.47	10.1	2.60	930	7.2	27.1
Silicon.....	0.32	11.4	2.42	1733	2.3	28.3
Phosphorus, red....	9.2	14.4	2.15	863 ²	?	31.04
Phosphorus, white..	20.5	16.6	1.82	317	36.0	31.04
Sulfur.....	12.9	15.5	2.07	384	18.0	32.07
Chlorine.....	[95](?)	25.0*	1.42*	171	35.46
Potassium.....	31.7	45.5	0.862	335	25.0	39.10
Calcium.....	5.7	25.3	1.53	1073	40.07
Chromium.....	0.9	7.7	7.06	1823	52.0
Manganese.....	0.84	7.7	7.37	1533	54.93
Iron.....	0.60	7.1	7.85	1790	3.6	55.84
Nickel.....	0.43	6.7	8.7	1725	4.2	58.68
Copper.....	0.75	7.1	8.92	1356	5.0	63.57
Zinc.....	1.7	9.5	7.13	692	8.7(?)	65.37
Arsenic.....	4.5	13.3	7.53	1073	1.6	74.96
Selenium.....	12.0	18.5	4.28	490	13.0	79.2
Bromine.....	52.	25.1	3.12	266	79.92
Rubidium.....	40.	56.0	1.53	312	[30](?)	85.45
Molybdenum.....	0.46	11.1	10.23	2773	1.1	96.0
Palladium.....	0.54	9.3	12.13	1822	3.8	106.7
Silver.....	1.01	10.3	10.5	1234	5.7	107.88
Cadmium.....	2.1	13.0	8.60	594	7.4	112.40
Tin.....	1.9	16.2	7.29	505	6.7	119.0
Antimony.....	2.4	17.9	6.71	903	3.3	120.2
Iodine.....	13.0	25.7	4.94	386	25.0	126.92
Cesium.....	61.	71.0	1.87	301	[33](?)	132.81
Tantalum.....	0.53	10.9	16.67	3123	2.3	181.5
Tungsten.....	0.27	9.6	19.23	3300(?)	1.1	184.0
Platinum.....	0.38	9.1	21.31	2020	2.7	195.2
Gold.....	0.64	10.2	19.24	1336	4.3	197.2
Mercury.....	3.95	14.8	13.55	234	18.	200.6
Thallium.....	2.3	17.2	11.83	574	9.0	204.0
Lead.....	2.33	18.2	11.37	600	8.8	207.2
Bismuth.....	3.0	21.2	9.80	543	4.0	208.0

¹ Personal communication from Dr. Weintraub.² Smits and Bokhorst, *Amst. Acad.*, 17, 969 (1915).

be shown to have relations with each of these data. The values for melting points and coefficient of expansion were most of them taken from the Landolt-Börnstein Tables (1912). Nearly all the other data (including most of the atomic weights) were determined at Harvard. The numbers given in brackets [] were not determined directly, but have been approximately calculated on the basis of analogous data. The coefficients of expansion of solid cesium and rubidium are estimated roughly, assuming that the difference between the solid and liquid form is about the same in the case of cesium as in that of potassium, and that the value for rubidium is, approximately, half way between that of potassium and cesium. These estimates are sufficiently exact for the purpose in hand. Cubic coefficients of expansion are taken as 3α ,—the letter α designating linear coefficients.

It is interesting and satisfactory that such of these results for compressibility as concern the elements studied by Grüneisen are now in reasonable accord with the results obtained by him with the help of the theory of elasticity, as already pointed out in the joint paper with E. P. Bartlett. The comparison with the scanty work of others, as shown by the figures on the 48th page of the Landolt-Börnstein Tables (1912), also shows so good an agreement that there is every reason to believe the figures given above to represent closely the true values of the constants in question. Therefore, they are worthy of further study, especially as regards their mutual relations and their relations to other properties.

On comparing the results concerning compressibility with one another, the first point to which attention may be called is the fact that three of the elements included in the table are in the liquid condition, namely, chlorine, bromine and mercury. This fact prevents the compressibilities of these substances from being strictly comparable with those of the others, because the available evidence seems to show that at the same temperature liquids are usually much more compressible than the solids crystallized from them. At the time of publishing the early work, this fact, although suspected, could not be definitely stated, because no measurements had ever been capable of proving the point; but since that time data concerning several cases have been obtained.

The first published and perhaps the most striking of these is the comparison of the compressibility of common ice and water, especially because ice, having the greater bulk, might be supposed to show a greater compressibility than liquid water, if such a contingency were ever possible. Nevertheless, investigation has shown that the compressibility of ice is only about one-quarter of that of water at neighboring temperatures.¹ Other cases are those of *o*- and *p*-cresol, substances which likewise can be conveniently investigated both in the solid and the super-

¹ Richards and Speyers, *THIS JOURNAL*, 36, 491 (1914).

cooled liquid condition at neighboring temperatures. These determinations, not previously published, were carried out several years ago in Boylston Hall, Cambridge, with the help of J. H. Mathews. Solid *o*-cresol, having the density 1.0176 at 20°, was found to possess the average compressibility between 300 and 500 megabars of 23.8×10^{-6} ; and solid *p*-cresol, having the density 1.389 at 20°, was found to possess the average compressibility between 300 and 500 megabars of 21.8×10^{-6} , not much over half the values for the compressibilities of these substances in the supercooled liquid state over the same range (42.1 and 41.8).¹ These results are strikingly confirmed by results since obtained by Bridgman with the help of an indirect thermodynamic method.² He found as a minimum value for the difference between the compressibilities of solid and liquid orthocresol under 1 atmosphere's pressure the quantity 0.0000191 (reduced to the megabar standard), almost exactly in concordance with the difference between the values given above, considering that our determinations were made at a higher pressure. The more recent work of Harry Essex³ on solid and liquid benzene points in the same direction, for he found these to be 0.000077 and 0.000025, respectively. Bridgman's indirect method confirms these observations by predicting a difference between these two data of 0.00005. Thus the compressibility of solid benzene is only about one-third of that of the liquid.

Evidently, then, the compressibility of *solid* chlorine is not likely to be over 50×10^{-6} , and might be as low as 25×10^{-6} , or less than that of potassium. It is, moreover, fairly certain that the compressibility of solid bromine must be under 30×10^{-6} , or distinctly less than that of rubidium, while that of solid mercury is doubtless less than that of liquid mercury.⁴ Although, therefore, the evidence is fairly conclusive, it is perhaps safest to omit these liquids from the comparisons. Let us, then, plot the compressibilities of the usually solid elements in relation to their atomic weights in a curve more or less parallel to the corresponding values of the several atomic volumes, in the manner depicted in the early paper and again in the Faraday lecture of 1911.⁵ In the diagram, the low-

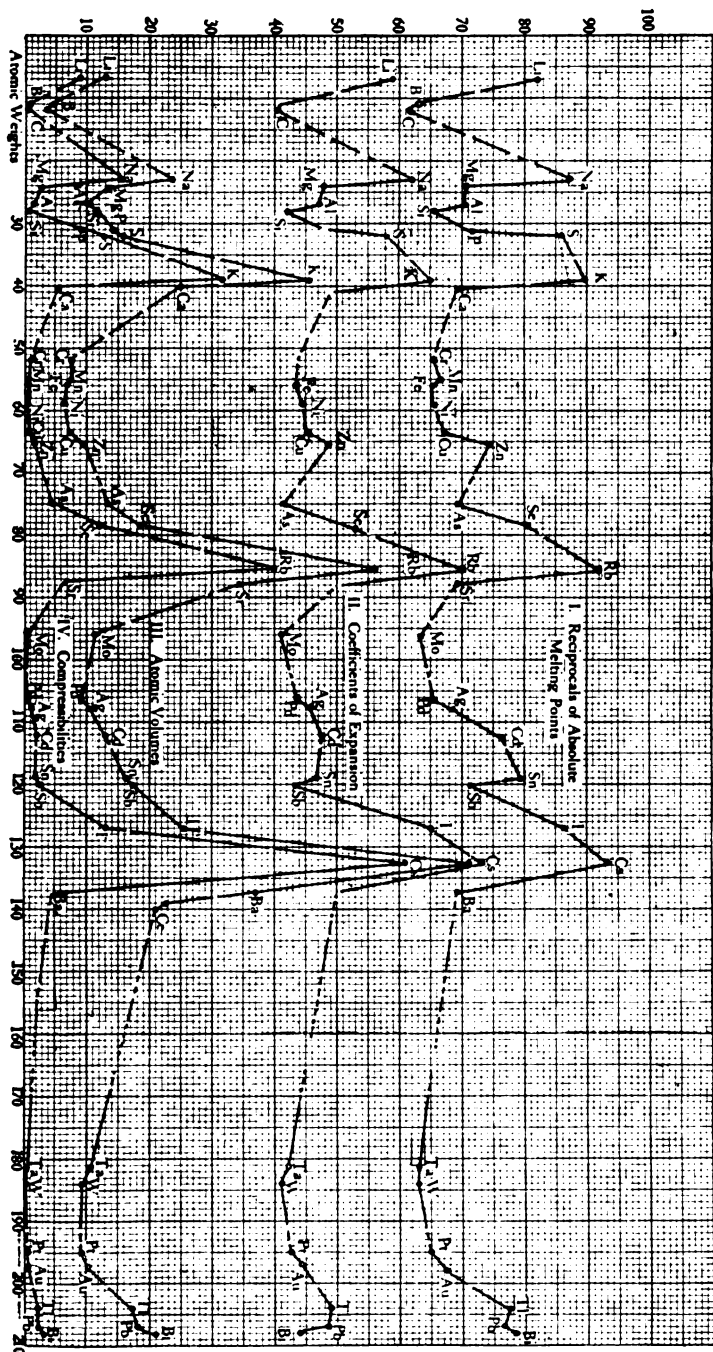
¹ Richards, Stull, Mathews and Speyers, *THIS JOURNAL*, 34, 989 (1912).

² Bridgman, *Phys. Rev.* (1915).

³ Harry Essex, Doctor's Dissertation, Göttingen, 1914. *Z. anorg. Chem.*, 88, 190 (1914). The values are both those found at 20°.

⁴ Bridgman, *Proc. Am. Acad.*, 47, 423 (1911). The difference between the compressibilities of solid and liquid mercury seems to be less than that in the other cases, perhaps because of its simple molecular structure.

⁵ "The Fundamental Properties of the Elements," *Science*, 34, 537 (1911). According to an unpublished suggestion of Professor Bridgman, these properties might equally well be plotted in relation to the *atomic numbers* instead of atomic weights. The curves thus plotted are perhaps a little smoother than the ones given, but are essentially similar. The idea of atomic numbers was probably first suggested by J. A. R. Newlands (*Chem. News*, 10, 94 (1864)).



PROPERTIES OF THIRTY-FIVE SOLID ELEMENTS.

Atomic weights are plotted as abscissae, other properties as ordinates.

Curve I represents reciprocals of absolute melting points, being plotted as $\frac{10,000}{T_m} + 60$.

Curve II represents cubic coefficients of expansion, being plotted as $300,000 \alpha + 40$.

Curve III depicts atomic volumes.

Curve IV depicts compressibilities, multiplied by one million.

est curve of all represents compressibilities and the one just above it, atomic volumes. To these have been added a curve depicting the coefficients of expansion (Curve II, next above the atomic volume curve) and another (Curve I) giving the reciprocals of the melting points (expressed in terms of absolute temperature¹) for reasons which will soon be apparent. To avoid complication in the diagram, only the denser forms of carbon and phosphorus are depicted in the curves; if white phosphorus had been included, it would have made a marked subsidiary peak in each curve—all of the properties here depicted being consistently represented by much larger values in the case of white phosphorus than in that of red phosphorus. In most cases no attempt is made to indicate the properties of other intervening elements not included in the table above. The omissions are indicated in each case of brief gaps in the curves, which may easily be identified by the atomic weights.

Let us now examine these curves in more detail. Turning first to the relation between the two lowest lines, representing atomic volumes (Curve III) and compressibilities (Curve IV), it is clear, as it was in 1907, that, roughly speaking, solids with large atomic volumes have large compressibilities. The new additions, tantalum and tungsten (each of which possesses very small atomic volume considering its high atomic weight), are seen, consistently, to possess also very small compressibilities, as would be expected. The relation of the newly determined boron to each of the varieties of carbon also corresponds to this rule; its compressibility and atomic volume are probably both greater than that of diamond, but both less than that of graphite.

Not only these two curves show signs of relationship, however. The likeness of the two upper curves to one another is very striking—this shows, of course, that in general, substances with low melting points have large coefficients of expansion—a fact in general long known, although the striking similarity of the curves is less familiar. Moreover, both of these upper curves, consistently with the two lower curves, likewise show peaks with the alkali metals and valleys with the heavier metals, although the subordinate convolutions are much more prominent in the two upper curves than in the lower ones.

A glance at the four curves at once suggests that there must be a fundamental connection between all these properties; and their close parallelism tempts one to seek a mathematical relationship between them, in spite of the inevitable complexity of the situation and the interdependence of each property not only upon each other of these, but also on many others. A preliminary attempt has been made to find such a relation-

¹ Attention is called to the interesting significance of absolute melting points as pointed out by Sudwik (*Z. physik. Chem.*, **88**, 632 (1914)).

ship, and although the outcome is not especially satisfactory, it is, perhaps, worth a brief recounting.

In the first place, one immediately concludes that atomic volume is not the only dimension which determines compressibility; since, for example, sodium and calcium, which have nearly the same atomic volumes, have widely different compressibilities. Silver and gold show like deviations. What other properties are concerned? Qualitative search among the data quickly leads to the conclusion that density is not quite adequately represented by its occurrence in the expression of atomic volume. In many cases, even with like atomic volumes, the denser element has the lesser compressibility. Again, those substances which are easily melted or volatilized seem to have a larger compressibility than would be warranted by their atomic volumes and densities; one is driven to infer that the compressibility of a solid is much increased by lowness of its melting point.

To make the matter more explicit, a few specific cases may be cited. For example as already stated, gold and silver have nearly the same atomic volumes; and they possess also nearly equal melting points. They have different densities, however, and the denser is the less compressible. This seems to be a general characteristic, which can be traced in many other places in the table.

Again, as has already been mentioned, sodium and calcium have nearly the same atomic volumes, and not very different densities, but they have very different melting points. Here it appears that the substance with the higher melting point (namely, calcium) has a much lower compressibility. A similar comparison may be made between copper and iron, although the difference is here not so marked. Comparing zinc and palladium, we find that greater density and higher melting point are both associated in palladium with a much lower compressibility than that of zinc.

On the other hand, sodium and potassium have nearly the same density and melting point, but their atomic volumes are very different. In this case and in many other cases otherwise similar, the compressibilities are nearly proportional to the atomic volumes (that is, to the atomic weights divided by the densities).

Bearing these facts in mind and noticing also that substances like cesium and phosphorus, which melt very near the temperature of experimentation, have abnormally large compressibilities, several attempts were made to formulate definitely the relationship, but, as was expected, no exact equation was found. The various attempts may all be represented by the general expression:

$$\beta = K f_1(A) / f_2(D) f_3(T_m), \quad (1)$$

when β = compressibility, A = atomic weight, T_m = absolute melting

point, K an empirical constant, and f_1 , f_2 and f_3 various functions of the quantities in question. The simplest of these trial equations giving reasonably good results took the following form:

$$\beta = 0.00021 \frac{A}{D^{1.25} (T_m - 50^\circ)} \quad (2)$$

A few of the best agreeing values, thus calculated (arranged according to the natural groups of the elements, and compared with the actual values) are given in the table below:

COMPRESSIBILITIES, CALCULATED AND FOUND.

(Each multiplied by one million.)

	Calc.	Found.		Calc.	Found.
Lithium.....	8.0	9.0	Magnesium.....	2.8	2.9
Sodium.....	15.6	15.6	Zinc.....	1.9	1.7
Potassium.....	34.0	31.7	Cadmium.....	2.9	2.1
Rubidium.....	40.0	40.0	Molybdenum.....	0.50	0.46
Cesium.....	52.0	60.0	Tungsten.....	0.29	0.27
Copper.....	0.66	0.75	Iron.....	0.52	0.60
Silver.....	1.02	1.01	Palladium.....	0.60	0.54
Gold.....	0.79	0.64	Platinum.....	0.46	0.38

This is a moderately good showing, and although some of the other elements are more divergent (especially silicon, where the calculated value is nearly four times as great as the observed value) nevertheless, all of the figures are of the right order of magnitude. Considering that the atomic weights range from 7 to 208, the densities from 0.53 to 21.3, the melting points from 28° to 4000° or over, and the compressibilities from 0.27 to 60 (over two hundredfold the lowest), this degree of consistency is perhaps as good as could be expected.

It is perhaps worthy of note that some of the elements giving discrepant results also give discrepant results with regard to the law of Dulong and Petit—namely, silicon, phosphorus, sulfur, as well as carbon, for which the calculated values of the compressibilities are, respectively: 1.2, 14, 8.2 and 0.13. There is perhaps a tendency toward a specific value for the "constant" K with each group of elements; for instance, to take a widely divergent group, since sulfur and selenium give (with $K = 0.00021$ as above) theoretical values only on the average about 56% of the observed values, the assumption $K = 0.00038$ would have given satisfactory values for these nonmetals, and perhaps also for tellurium. Bearing this in mind, one may perhaps be able to predict the values of the compressibilities even in a group behaving abnormally if one member of the group is known.

To return to a more normal group, it is clear that the prediction of the approximate compressibility of strontium and barium, for example (elements not yet subjected to experimental investigation as regards this

property), becomes a very simple matter. On substituting in the trial equation found above the values for the densities and melting points of these elements as found by Guntz, the compressibility of strontium is calculated to be over 0.000006 and that of barium 0.000004. Because the value for calcium calculated in the same way is not very far from the observed fact (0.000005 instead of 0.000006) one has a right to infer that these predicted figures also are not very far from the truth. An actual case of verified prediction is that of boron, which was computed from the equation to be 0.29×10^{-6} and was afterwards found to be 0.30×10^{-6} .

In the table (p. 1652) giving the calculated values for several groups of elements, and also among other groups, it is noticeable that (except in the case of cesium) the equation gives too high values with the larger atomic weights. This could be corrected, of course, by raising the quantity A to a fractional power. The equation $\beta = 0.00067 A^{0.75}/D^{1.25}(T_m - 50^\circ)$ gives much better results for copper, silver, gold, iron, platinum and all the heavier elements, but not such good results for the alkali metals. Therefore, it seems not worth while thus to complicate the equation for the present, until more is known about the quantitative effect of each unknown tendency among those which determine the magnitude of compressibility.

A somewhat similar equation based upon coefficients of expansion, instead of the reciprocals of the absolute melting point, could obviously be constructed, since the general shapes of the two curves are so similar; but hardly enough values are known for coefficients of expansion to make this profitable at the present time. The parallelism may be supposed to arise because each of these properties (namely, the tendency to melt and the tendency to expand on heating) may be referred to the same fundamental cause, each being increased by lack of cohesion.

No pretense is made that the foregoing equation is an exact statement of all the many-sided bearings of compressibility, and doubtless a better equation could be devised, if one assumed more complicated functions; but for the present the further pursuit of the quest seemed not worth the necessary time. It is at least of interest that an expression has been found capable of giving the approximate order of magnitude of the compressibilities of different substances, computed from the atomic weights, densities and melting points; this seems to show that the basis of the equation really represents some of the more important tendencies which are at work.

Attention may be called to the fact that the general nature of the equation is somewhat similar to that of the equation of Dupré, which gives, with fair approximation, the compressibility of numerous carbon compounds, namely (at constant temperature), $\beta = K \alpha/D^2$, the chief difference being that the effect of diminishing cohesiveness is expressed in one case

by increase of $1/f_2(T_m)$ and in the other case by increase of α (the coefficient of expansion)¹—the other two quantities being closely parallel, as has been shown. The equation of Dupré, however, seems to put somewhat too much emphasis upon density to be applied to the elements.

The comparison of the new empirical equation with the outcome of recent considerations by Grüneisen is not without interest, although the latter applies only to "monatomic" elements. He advanced a hypothesis assuming that a monatomic solid substance always melts when its volume is increased by a definite fraction δ above that which it occupies at the absolute zero;² that is to say, when

$$\frac{v_m - v_0}{v_0} = \delta = 0.08 \text{ approximately,} \quad (3)$$

in which v_m is the atomic volume at the melting point and v_0 is the atomic volume at the absolute zero.

From this equation, which he supported empirically, he evolved the expression:

$$\frac{1}{T_m} \left(\frac{dT_m}{dp} \right) = (n + 2) \beta_0 \frac{1}{q}, \quad (4)$$

in which T_m is the absolute melting point, n a constant (approximately 4), β_0 the compressibility of the element the absolute zero (not very different from that at the temperature of the room), and q the ratio of the coefficient of expansion at the melting point to the average coefficient of expansion, as follows:

$$q = \left(\frac{\partial v}{\partial T} \right)_{T_m} : \left(\frac{\partial v}{\partial T} \right)_{0 \dots T_m} \quad (5)$$

Equation 4 is in a form into which it is possible to introduce the Clapeyron-Clausius equation for gram-atomic latent heat of melting (Q). Making this substitution and designating the change of atomic volume upon melting by $V'_m - V_m$, Grüneisen obtained the expression:

$$Q = \frac{V'_m - V_m}{(n + 2) \beta_0} q \quad (6)$$

In this form Grüneisen's equation does not seem, at first sight, to be closely related with the new empirical equation (2) above; but by substituting for the latent heat of melting (Q) a quantity found empirically by J. W. Richards in 1897:³

¹ Perhaps the most careful recent study of coefficient of expansion is that of Grüneisen (*Ann. Physik.*, [4] 33, 33 (1910)), who compares many of the values with the equation of Thiesen, *Verh. deutsch. physik. Ges.*, 10, 410 (1908). See also *Ann. Physik.*, [4] 26, 393 (1908).

² *Verh. deutsch. physik. Ges.*, 14, 330 (1912). Needless to say, it is not always easy to decide whether a solid element is monatomic or not.

³ Richards, *Chemical News*, 75, 278 (1897).

$$Q = 2.1T_m \text{ or plausibly } Q = 1.06RT_m,$$

and transposing the equation, we obtain the following:

$$\beta_0 = \frac{V'_m - V_m}{1.06(n + 2)RT_m} q \quad (7)$$

Now, taking account of the fact that n is nearly a constant, and that q probably never varies far beyond the limits 1.2 and 1.5, we may combine all these quantities with R in K and write approximately:

$$\beta_0 = K \frac{V'_m - V_m}{T_m} \quad (8)$$

That Equation 8 is not general is shown by the fact that it gives a negative (and therefore impossible) compressibility for bismuth; but bismuth is probably not monatomic, and therefore would not come within Grüneisen's moderate claim. Nevertheless, Equation 8 is seen to point with monatomic elements in the same direction as the new empirical equation (2) above, for the absolute melting point finds its place in the denominator in (8) as well as in (2), and the numerator in (8) contains the difference between the atomic volumes in the solid and liquid condition. This would naturally be greater, as a rule, the greater the atomic volume, which occupies the numerator in Equation 2. To give four values selected at random, the values for $V'_m - V_m$ for lead, sodium, potassium, and cesium are, respectively, 0.6, 0.6, 1.2, and 2.0, while the atomic volumes are the nearly proportional figures, respectively, 18.2, 23.7, 45.5 and 71. Hardly enough values for $V'_m - V_m$ are known to trace the possible slight additional effect of varying density; but the general similarity of Equations 8 and 2 is clear. Of the two, Equation 2 seems to be the better, not only because it never leads to an absurdity with substances solid at 20° C., but also because data for it are plentifully at hand.

The further comparison of these considerations with the well-known recent molecular theory of solid bodies of Einstein, Debye, Grüneisen, and others, would be a matter of interest, but will be deferred to another occasion. It will be remembered that this theory is based upon certain assumptions concerning the relation of energy and frequency of hypothetical internal atomic oscillations to specific heat and other thermodynamic properties. For a brief but fairly recent interesting review of this work, the reader may be referred to Grüneisen's recent brochure.¹

Attention may be called to the fact that the tendencies depicted by Equation 2 are, in a general way, those which would be expected from the prediction of the theory of compressible atoms. An atom much distended because of a loose internal makeup might be supposed to be

¹ Grüneisen's "Molekulartheorie der Festen Körper," 1913. Professor E. W. Washburn has kindly suggested in a private communication the interest of such a comparison of the new approximate empirical equation with the hypothetical ones.

highly compressible; and so might one much distended because not greatly pressed upon by outside cohesive pressure. Both of these tendencies would cause small density and accordingly large atomic volume; and the second of these tendencies would add low melting point. Therefore, the general form of the equation is plausible.

The case of tungsten is especially striking. The atomic volume is small, considering its large atomic weight (that is to say, its density is great) and its melting and boiling points are so high that this metal is now chosen as the most suitable for the filaments of electric lights. All these properties would seem to indicate cohesiveness; and a body under the pressure of such extremely high cohesion would be supposed to have a very small compressibility, which as a matter of fact it has—the value being 0.00000027, the smallest of any element thus far carefully studied.

In conclusion, the contents of this paper may be summarized by stating that the compressibilities of all the 38 elements determined at Harvard have been reduced to the new standard for the compressibility of mercury as determined at the Jefferson Physical Laboratory and the Wolcott Gibbs Memorial Laboratory of Harvard University. The new values for the compressibilities are now in accord with the less extended work of Bridgman, Grüneisen, and others. Attention is directed to probable relations between the compressibilities and the atomic volumes, densities, coefficients of expansion, and melting and boiling points of many of these elementary substances; and an approximate empirical equation is proposed for the calculation of these compressibilities.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE SURFACE TENSIONS OF WATER, METHYL, ETHYL AND ISOBUTYL ALCOHOLS, ETHYL BUTYRATE, BENZENE AND TOLUENE.

BY THEODORE W. RICHARDS AND LESLIE B. COOMBS.

Received May 5, 1915.

This investigation is a part of a series of investigations having for their object the study of the fundamental properties of liquids. It is hoped that when a number of these properties have been determined with great accuracy, the essential relations between them may be discovered with greater certainty than is possible at present.

A glance at the published data¹ concerning surface tension leads one to conclude that much remains to be done. For example, the values

¹ See, for example, "Landolt-Börnstein Tabellen," p. 113 (1912). The recent interesting research of Morgan upon the drop-method has developed since that time (THIS JOURNAL, 30, 360 (1908), and many other references given in THIS JOURNAL.

obtained by experienced men for water at 20° vary all the way from 70.6 to 78, according to different methods. Even a single method, that of the rise in capillary tubes, has yielded results in the last twenty-five years varying from 70.6 to 72.7, and no satisfactory evidence is forthcoming as to the reasons for the difference.

To us it seemed, therefore, worth while, not only to study the surface tension of a variety of new liquids, but also to discover the reason for the divergences between different methods, and to obtain results of absolute as well as of relative accuracy for liquids already studied. The present paper is a preliminary attempt, which seems to have been successful in locating several of the heretofore not quite adequately heeded sources of error.

The method chosen was that of measuring the rise of liquid in capillary tubes, because this method seems to be one of the most direct and least likely to lead to insoluble mathematical complications. The method has been used by many experimenters in the past.¹ No attempt will be made to give a complete discussion of older work, partly because some of the papers are not at present accessible, except in the form of abstracts; and partly because it is difficult to do justice in the limited space available here; but from time to time special points in some of these papers will be mentioned in comparison with our own procedure.

There are, of course, a number of minutiae which may affect the accuracy of the outcome. Prominent among the points needing detailed consideration were the following: First, the precise determination of the diameter of the tubes; secondly, the method of determining the exact position of the bottom of the meniscus; thirdly, the discovery of the diameter necessary in order to attain the flat surface with which the capillary rise is to be compared; fourthly, the precise determination of the weight of liquid contained in the meniscus at the top of the capillary tube; and fifthly, the angle of contact of the liquid with the tube. These points are discussed in order below.

The Diameter of the Capillary Tubes.

This question involved nothing not already well known. Each capillary tube was selected as follows: An apparently suitable piece of tubing 35, 1821 (1913)). The work of Renard and Guye should also be noticed: *J. chim. phys.*, 5, 81 (1907), and that of Kistjakovsky, *Z. Electrochem.*, 8, 376 (1902); 12, 513 (1906).

¹ For a summary of Quincke's very irregular results and a bibliography of his eleven papers, the reader is referred to "Landolt and Börnstein's Tabellen," pp. 103, 116 (1905). The method has also been used by Ramsay and Shields, *Z. physik. chem.*, 12, 433 (1893); Weinstein, "Landolt and Börnstein's Tabellen," p. 113 (1912), quoted from *Metron. Beitr. No. 6 Norm. Eich.-Komm.*, 1889; Domke, *Ibid.*, quoted from *Abh. Eich.-Komm.*, III, p. 3, 1902; Grabowsky, Dissertation, Königsberg (1904). Renard and Guye (*Loc. cit.*) and many others.

was carefully cleaned with concentrated sulfuric acid and dichromate, washed with distilled water and carefully dried. A thread of pure mercury was introduced into it and the length of this thread was exactly measured by means of an accurate comparator or calibrating instrument, the magnification of the microscope of which was so high that 12.50 turns of the micrometer head equaled 1 mm. The tube was placed beside a rod graduated in millimeters (verified by the Bureau of Standards) and the readings were transferred by swinging the axis of the microscope. Next, the thread was moved, again and again, along the tube; and its length was each time remeasured. In a tube of uniform bore the various lengths should, of course, be equal. After very many pieces of tubing had been examined, two were found sufficiently uniform for the purpose of this work; the extreme values for the measured lengths differed by less than 1 part in 2000. In one of these tubes the average length of a thread of mercury weighing 0.8650 g. was thus found to be 20.47 mm., and subtracting from this length the correction of 0.54 mm. for the protrusion of the two meniscuses,¹ the corrected length 19.93 mm. of the cylinder of mercury was found, and hence its radius according to equation: $r = \sqrt{0.8650/13.546 \pi 19.93} = 1.0099$ mm. This tube was used in Apparatus III.

Another tube, which was only about one-fifth the diameter of this, served in Apparatus IV. In it 0.3403 g. of mercury occupied 213.31 mm. — 0.04 mm. (correction for two meniscuses)² = 213.27 mm., hence its radius was 0.1936 mm. It had been tested throughout its length by a short column of mercury in the same way as the other wider tube. This calibration tested not only equality of bore, but also the essential evenness of the glass walls—a very important matter, as will be seen.

At about the center of each capillary tube was etched a fine mark, which served as a reference mark, so that it was possible to fill the apparatus, if need be, to exactly the same point in successive settings. The tubes were fused to other parts to be described later.

The Lighting and Observation of the Meniscus.

The second point may now receive consideration. Our tubes containing the liquid to be studied were placed in a square thermostat tank, with windows in front and behind. For defining and measuring the meniscus we used a development of the method long used for reading both burets and barometers. A movable black metal screen with a sharp horizontal upper edge was immersed in the thermostat tank, just

¹ L. W. Winkler, *Z. angew. Chem.*, p. 719 (1903); *Z. anal. Chem.*, 40, 403 (1901).

² The smallest diameter measured by Winkler was 1 mm., but his results are so consistent that they may safely be extrapolated to zero diameter, where the height of the meniscus also would be zero. On this basis the correction for a tube 0.2 mm. in diameter is found to be 0.02 mm., which is doubled for the two meniscuses above.

behind the tubes to be observed. This screen could be adjusted at any height at the will of the operator by means of a delicate mechanism consisting of a fine chain passing over a pulley and around a drum held by a variable friction clutch. When the screen had been raised until its edge appeared to be exactly tangent to the deepest point of the meniscus, the area of the meniscus was wholly darkened and its lower contour became entirely clear and sharp. The apparatus thus adjusted is shown in the photograph, Fig. 1. There is every reason to believe that the edge thus observed is the true boundary of the meniscus, and in all the work to be described, the above relative position of window, screen, apparatus and carefully leveled cathetometer - telescope was maintained.

The Necessary Diameter of the Wide Tube.

Turning now to the third point mentioned above, one soon finds, on studying earlier work, that not all of the experimenters have agreed as to the width necessary. Even in the best laboratory handbooks¹ the directions are somewhat vague. Magie,² working by another method under Helmholtz's direction, speaks of employing a tube 3 centimeters in diameter, but others have usually employed a smaller tube. The best of the recent work in this respect seems to have been that of Walden and Swinne.³ Like Magie, they used a tube 3 cm. in diameter, but they admit that this was probably not quite large enough, and calculated a possible correction with the help of a somewhat doubtful equation of Desains. The assumption seems to have been usually made that a tube 2 cm. in diameter is wide enough.

On the other hand, it had become clear to one of us in preliminary investigations conducted some years ago with the help of the late Dr. C. L. Speyers that this question had been by no means settled. The

¹ See for example, Ostwald-Luther. On page 237 the statement is made that the tube should be "recht weit" (1912).

² Magie, *Wied. Ann.*, 25, 421 (1885).

³ *Z. physik. Chem.*, 79, 700 (1912).



Fig. 1.—Photograph of Apparatus III in thermostat tank. The screen behind the tube is raised so as to be exactly tangent with the meniscus (about half actual size).

familiar fact that a drop of insoluble oil (such as that which separates from the dilute emulsion of "Sulphonaphthol") on water in a bottle will seek exactly the center unless the bottle is 4 to 5 cm. in diameter seems to suggest that there is a real depression, even in a fairly large surface, when it is surrounded by walls wet with the liquid. For an accurate estimation of the surface tension, the larger tube should obviously contain a perfectly flat surface; but we cannot find that the diameter necessary to insure this condition has ever been adequately investigated. The matter, although apparently simple, is not after all very easily tested because of the usual inequalities in the glass walls of wide tubes. A slightly prismatic vertical section of wall (that is, a wall thicker at one end of the tube than at the other) causes considerable shifting of the image. Moreover, it is necessary that both tubes to be compared should be in a perfectly vertical position, for otherwise the greater refractive index of the glass causes an important displacement. If one of the tubes is slightly inclined to the other, or if one of them is slightly thicker at one end, the effect of difference of level might appear when really none existed. The two tubes must be kept at exactly the same temperature, for obvious reasons.

Our first arrangement for testing the flatness of liquid surfaces in large tubes consisted in a three-fingered or double U tube, having its three fingers, respectively, 2.1, 2.54 and 3.8 cm. in diameter, which was partly immersed in the thermostat tank mentioned above. This tank consisted of a copper, tin-lined box, $25 \times 25 \times 30$ cm. It was provided, as before stated, with two windows; of these, that at the back of the tank was made of common glass; but the other, opposite to it, at the front, was provided with optically ground plane glass, in order that no distortion, due to the irregularities always present in ordinary glass, might cause error in the readings. Of course both of these windows were placed near the top of the tank.

The regulator was of the ordinary toluene-mercury type, having two fingers; it easily kept the bath constant to within 0.01° . The bath was set at 20.0° , since many other physical properties have been determined at that temperature. There were also the customary devices for heating (by electricity), cooling by a slow current of cool water, and thoroughly stirring the water in the thermostat.

The double U-tube (see Fig. 2) was filled two-thirds full of distilled water and set in the thermostat, exactly vertically, by means of a plumb-line. The levels of the water within the tube were, of course, sufficiently below the water level of the thermostat so that the menisci could be readily observed through the telescope of the cathetometer.

Proceeding with the comparison of the three menisci in the U-tube, we observed immediately that the smallest tube of 2.1 cm. diameter

not only did not have a plane surface at the center of its meniscus, but also that it produced an appreciable rise of the water level above that of the largest tube. Therefore, because it was obviously too small, no further attention was paid to this tube. The large and medium tubes were very carefully compared. Not only were measurements taken with one side of the apparatus presented to the telescope, but also settings were made again after the tubes had been rotated in the horizontal plane through 180° . Thus by observing the meniscus through the two sides of the apparatus it was hoped to eliminate, or at least detect, any errors due to irregularities in the walls of the glass tubes. Afterwards more water was added and another set of readings made, the observations, of course, in this last case being made through a still different part of the glass walls. Before each reading was taken, the apparatus was inclined, so that the glass walls were well wetted above the meniscus, then clamped exactly vertically, and five minutes were allowed for complete drainage of the liquid from the walls of the tube, before readings were taken. Great care was taken to always have the cathetometer-telescope and column properly levelled.

In making the measurement the fixed cross hair of the telescope was set on the largest meniscus, the telescope swung through a small arc, and the movable hair adjusted to the next smaller meniscus. Thus the difference in level of the menisci was recorded in terms of turns of the micrometer screw on the telescope. By later substituting a standard rule for the apparatus, the number of turns of the micrometer head corresponding to 1 mm. of the standard rule was determined.

In a preliminary series of not very concordant determinations, it was thus found that when viewed from one side, the largest meniscus appeared to be -0.09 turn of the micrometer lower than the middle one, and when viewed from the other side -0.14 ; average, 0.11 turn. Since 1 turn of the micrometer head was found to equal 0.67 mm., the difference in level between the lowest points in the menisci was 0.073 mm. It should be noted that there was a difference of 0.03 mm. between the observations made on the two sides of the tube. This was doubtless due to irregularities in the glass walls of the apparatus; the experimental error of setting should not be over 0.003 mm.

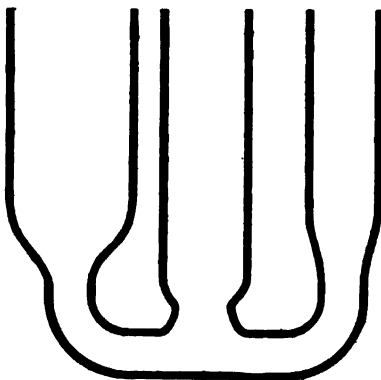


Fig. 2.—Diagrammatic section of double U-tube used for measuring levels in wide tubes (one-third actual size).

It occurred to us that if irregularity in the opposite walls of the tubes could cause such an error as appeared in these observations, there might be an error in both caused by a prismatic irregularity in both walls of one tube, an error which would not be eliminated by our simple precaution. A way to detect this error would be, of course, to invert the apparatus and make new settings; but this could not be done with the apparatus

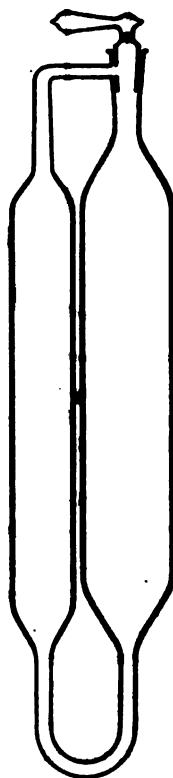


Fig. 3.—Diagrammatic section of reversible U-tube for discovering capillary effect in wide tubes (one-third actual size).

in the foregoing form. Hence in a new outfit a large U-tube with arms of unequal diameter was sealed at the top, and provided with a ground stopper for filling (Apparatus II, Fig. 3). With such an apparatus the tubes could be rotated not only through 180° horizontally, but also through 180° vertically. Thus any wedge-shaped places in the walls of the tube would become apparent; for by inverting the apparatus, keeping the same side always towards the telescope, identical readings could be obtained only if the surfaces of the tube were parallel. If the walls were wedge-shaped, readings would be obtained deviating from the truth in opposite directions. In this case the average would give the true value.

In this modified apparatus the large tube (I) had a diameter of 38 mm., the smaller (II) of 25.4 mm., *i. e.*, they were of exactly the same diameters as the large and medium tubes of the former apparatus. The glass was carefully chosen.

In every case the apparatus was set in a vertical position by means of a plumb-line and the menisci were carefully arranged, both exactly in focus of the telescope, which belonged to a first-rate, carefully leveled cathetometer. Two complete series were made, the apparatus being entirely dismantled between them. Adequate precautions as regards wetting of the walls of the tubes and drainage were carried out. The amount of water was so chosen that the water level came at exactly the same point on the large tube, no matter which position was adopted. The results of these experiments with pure water are tabulated in Table I. Readings were taken in four positions: Upright front (*a*), upright back (*b*), inverted front (*c*) and inverted back (*d*). The level in the larger tube was always set at 0.00 on the fixed spider-line of the cathetometer-telescope, and the readings of the level in the narrower tube, made with the movable spider-line, as already described, are recorded below in the table in fractions of a millimeter:

TABLE I.

	First series.	Second series.
Upright (a).....	0.110	0.116
(b).....	0.124	0.134
Inverted (c).....	0.110	0.133
(d).....	0.096	0.098
Average.....	0.110	0.120

From these readings it would appear that the front of the tubes (Readings *a* and *c*) possessed more nearly parallel-faced walls than the back (Readings *b* and *d*). Although the agreement is not perfect, it seemed, nevertheless, clear that the average of all the readings should give a value very near to the truth, and that the level of water in the tube of 25.4 mm. diameter was really 0.11 mm. higher than that in the tube of 38 mm. diameter.

The question then arose as to whether or not the tube of 38 mm. in diameter was large enough to obtain a perfectly flat surface. Of course, similar experiments could have been instituted with another reversible U-tube having one arm yet wider, but it proved to be difficult to obtain a sufficiently even tube of larger diameter. Moreover, qualitative observation seemed to show that 4 cm. is large enough. This observation was made in two ways: in the first place, the study of the meniscus in the experiment just recorded showed unquestionably that no part of the surface in the narrower tube (diameter, 25.4 mm.) was perfectly level. The curve was continuous from side to side. On the other hand, in the 38 mm. tube a portion in the middle, apparently about 5 mm. in length, appeared to be flat, coinciding exactly with the horizontal spider-line of the telescope. From this it would appear that a diameter 33 mm. might be enough, and that, therefore, 38 mm. should be ample. This conclusion is supported by observation of the reflection from the surface of water in a wider vessel. If a beaker of water 7 or 8 cm. in diameter is thoroughly cleaned, filled almost to the brim with pure water, and immersed in a large dish of water, the reflection in both surfaces of a vertical rod behind it is seen to be perfectly straight in the middle, but to bend when the image approaches nearer than about 1.7 cm. to the beaker wall. This indicates the need of a tube wider than 34 mm. A similar phenomenon is shown by mercury, of which a surface more than 40 mm. in diameter shows a small level spot in the center, approaching to within about 18 mm. of the edge. A surface less than 35 mm. in diameter shows no such level spot. These dimensions about coincide with those observed in the case of water. Therefore, we concluded that the error of level in a 38 mm. tube would be so small as to be outside the limit of our measurement. Accordingly, all our results recorded in the present paper were obtained with this large diameter—perhaps the widest unrestricted

tube which has ever been used in surface tension measurements. This matter will receive further study in order to discover if a yet wider tube may be necessary for the most exact result. At any rate, it is clear that any outcome obtained with the wider tube as narrow as 20 mm. must be far from the truth. This fact doubtless accounts, at least in part, for the low results for surface tension often obtained by this method.

The error is magnified by the presence of a further point of support in the middle of the wide tube, such as the capillary usually employed. In some preliminary experiments of our own, it was found that when a fine glass rod is immersed in water in the middle of a tube 20 mm. in diameter, the capillary rise in this tube is about 0.31 mm. more than that without the rod. Because liquid in a tube of this diameter, even without the central capillary, is distinctly above a level surface, it will be seen that

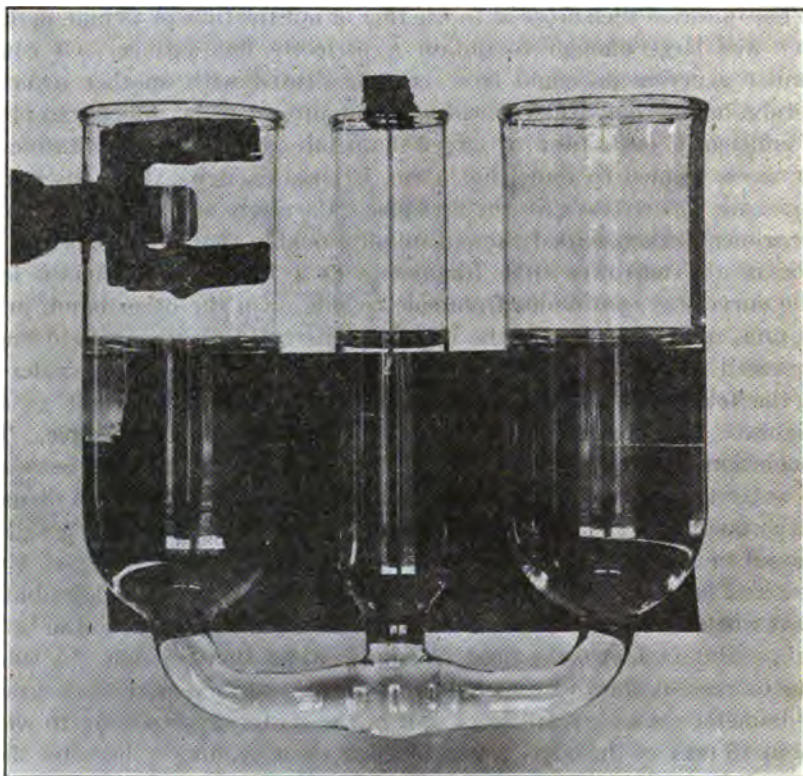


Fig. 4.—Photograph (seven-tenths actual size) of capillary rise in 20 mm. tube (with central rod) above level in two 36 mm. tubes. The straight-edged screen behind the tubes is exactly tangent to the larger menisci. This photograph shows the magnitude of the error in the usual surface tension apparatus, which is like that in the central tube.

the many experimenters who have used this arrangement must have obtained results much too low.

The combined effect is shown in the appended Fig. 4. This is a somewhat reduced photograph of a 20 mm. tube between two tubes, each 36 mm. in internal diameter. The middle tube has within it, in the center, a fine glass rod, which, as regards its exterior capillary action, would give the same effect as a fine capillary tube. The tube was carefully leveled and the lens of the camera placed exactly on a level with the menisci. A screen with a straight upper edge was then arranged behind the menisci in such a way as to be exactly tangent with the bottoms of the two larger ones. Any one can see how much the liquid in the middle 20 mm. tube is raised above the level in the wider tubes. This error, which does not need a micrometer to appreciate its magnitude, has entered into many of the earlier investigations, especially among the recent ones in that of Rénard and Guye.

The Correction for the Weight of the Meniscus in the Capillary.

The reading of the height in the capillary is made from the lowest point of the meniscus, and all the liquid above that level in the capillary, rising up to the walls of the tube, is, therefore, ignored in the simple reckoning. But the weight of the liquid in the meniscus itself may be very important unless the capillary is exceedingly fine.

The calculation of the exact shape of the meniscus is a mathematical problem of great intricacy, which has apparently not yet been satisfactorily solved.¹ Special assumptions have usually been introduced in order to effect integration, and terms of a smaller, but still possibly significant, order must be neglected. The usually assumed relation is that of Poisson,² who came mathematically to the conclusion that h is to be found as follows: $h = h_0 + r/3 - r^2/h_0 \cdot 0.1288$. This equation gives a reasonable result when the capillary is fine; but when the tube becomes wide, r^2 exerts too great an influence, and with a diameter approaching 1 cm., h becomes less than h_0 —an obvious absurdity. Hagen and Desains³ have proposed a widely different equation as follows: $h = h_0 + a^2 r / (3a^2 + r^2)$; in which a^2 is the capillarity-constant (the true height multiplied by the diameter of the tube). This expression (based upon La Place's reasoning) at least never makes the calculated value less than the observed value, and is, therefore, in this respect to be preferred to the

¹ La Place, Gauss, Young, Poisson, Maxwell, Rayleigh, Gibbs and others have attacked the problem. Lord Rayleigh's papers on the theory of capillarity are especially interesting. See Lord Rayleigh's collected works 1883-1892, II, 236, III, 397, 513, 562, 572 (1901). A historical and appreciative review of the work of these various investigators is forbidden by lack of space.

² Poisson, "Nouv. Théor. d. l'act. capill.," p. 110 (Paris, 1831).

³ Hagen and Desains, *Ann. chim. phys.*, [3] 51, 417 (1857); see also Chwolson's "Physik," Vol. I, p. 598 (German edition) where the equation is incorrectly given.

equation of Poisson; but it is doubtful if all the necessary quantities have been considered. However, the equation reduces to $h = h_0 + r/3$ when h is very large (that is, when r is very small) as it should to correspond to the facts.

In view of this failure of both the usually accepted equations under common conditions, we sought to discover, if possible, further experimental light upon this vexed question.

Even superficial observation shows at once that the meniscus in a very small tube is almost hemispherical, and that this hemisphere becomes more and more oblate or flattened as the tube becomes wider. Obviously the short diameter of this pseudo-oblate spheroid ought to be an important help in solving the riddle. The measurement of the height of the meniscus between its lowest point and the point of actual contact with the glass walls of the tube was, therefore, carried out; it proved to be easier than had been expected.

In our apparatus, with the dark screen tangent to the meniscus, although the lower surface of the meniscus is very sharply defined, the extreme upper edge cannot be very easily identified. A simple device made it possible to determine exactly the position of this upper edge, nevertheless. If the screen is gradually raised above the position of tangency, its image becomes at first much refracted and distorted by the curved surface; but, as the screen is raised higher, its image approaches straightness again, until at a definite position the edge of the screen appears again entirely straight. This straightness must be attained at the level where the liquid meniscus is exactly in contact with the walls of the tube. The cross hair of the telescope can then be accurately set on the edge of the meniscus and screen, thereby giving exactly the position of the upper boundary of the meniscus.

Careful measurement thus made showed the height of the meniscus in a perfectly clean tube 0.4 mm. in diameter to be very nearly equal to the radius of the tube, varying but slightly with different liquids. Thus the shape of the meniscus in a fine tube of this sort is nearly spherical. If this were exactly true, the correction would be simply $1/8$ its height, because a hemisphere occupies precisely two-thirds of the volume of the circumscribed cylinder. Practically, the deviations from this simple expression are so slight with tubes of this very small bore that they may be neglected. Thus in such a tube the third term of the second member of the theoretical equation of Poisson should become so small as to be negligible.

The height of the meniscus in wider tubes next deserved attention. In the way just described the height of water in a meniscus within a tube 2.02 mm. in diameter was found to be 0.964 mm., a value near that of the radius, but slightly less. It seemed highly probable that within the limit of error of experiment it would be safe here to assume that this menis-

cus was a slightly flattened sphere (or oblate spheroid) with its shortest radius 0.964, and that the volume of the concave mass of liquid enclosed between the hemispheroid and walls was to be found by multiplying πr^2 by one-third of its height. The various qualitative arguments which led to this conclusion need not be detailed, because a satisfactory quantitative support of the assumption is found in the data of Winkler,¹ determined by actually weighing the water in the meniscus. For such a tube the correction to the height given by Winkler is 0.32 mm. in very close agreement with one-third of the meniscus height, 0.321. Hence it seemed reasonable to use this simple method with other liquids and other tubes of small diameter. The equation, then, used throughout this paper for tubes of 2.02 mm. (or less) in diameter, is $h = h_o + h_m/3$, in which h = the true corrected height, h_o = observed height, and h_m = the height of the capillary-meniscus, as observed by the method described above. When the tube is very small this becomes approximately $h = h_o + r/3$, because h_m is then almost equal to r .

This equation, like that of Hagen and Desains, is evidently safer than that of Poisson, since it never leads to an absurdity, no matter how wide the tube may be; and with small tubes we have good reason to believe that it is better than either of the others. For tubes over 4 or 5 mm. in diameter, it doubtless needs modification. In a very wide tube, *e. g.*, of 30 millimeters, nearly all the liquid raised must be in the meniscus (measuring here with water about 4 mm. in height). In this case, the correction which should be applied to the bottom of the meniscus to obtain the corrected capillary rise (easily calculated to be about 1 mm.) would be about one-quarter of the meniscus height instead of one-third, as was found with very small tubes. It seems probable, then, that these two fractions (one-quarter and one-third) represent the limits of the variation of the correction for the meniscus as applied to the measured height of this raised mass of water, and that all values for tubes of less than 30 mm. diameter must lie between these rather close limits. The corrected value of the rise above the standard flat level in any tube less than 30 cm. in diameter would, therefore, be $h = h_o + nh_m$, where n varies from exactly one-third with very narrow tubes to about one-quarter with wide tubes. A more comprehensive study of the relation of the weight of the meniscus to its height will be carried out in the near future in this laboratory. For the present research this was not necessary, because only very narrow and very wide tubes were used, and each of these was treated adequately with the definite knowledge hereinbefore detailed.

The Angle of Contact.

This is a very important consideration, concerning which the evidence is conflicting. In this preliminary paper we have made no attempt to

¹ L. W. Winkler, *Z. angew. Chem.*, 1903, p. 719.

add to the knowledge of it. The angle of contact enters into the complete expression for calculating surface tension in the form of its cosine, and must, therefore, assume a value of $2^{\circ} 30'$ in order to affect the result by 0.1%. It is true that early indirect results by Quincke seemed to show that the angle of contact, even with water, was as much as 25° , which would affect the result to the extent of 10%. More recent results, however, have discredited these conclusions. There is good reason to believe that, although in the case of mercury (where the tube is not wetted by the liquid) the angle of contact is considerable and important, in all those cases where the tube is fully wetted by the liquid, this angle is reduced to zero. Attention is especially directed to the careful and thoughtful work of Magie,¹ who found that some of the assumptions underlying Quincke's mathematical work were incomplete (as has so often been the case in discussions of this kind) and that there is really no basis for believing, at least as far as Quincke's results go, that any appreciable angle of contact exists. Ramsay and Shields² bring forward a very ingenious piece of evidence in favor of this thesis. They show that a completely spherical bubble, which has exactly the diameter of a small vertical tube, will not rise, but that a spherical bubble with a very slightly less diameter will rise in the tube. Because the spherical bubble must have its periphery tangent to the tube, and when it just fits the tube practically consists of two menisci, one concludes that the menisci are exactly tangent.

Nevertheless, the question is not wholly answered; and we hope before long to have further evidence to advance concerning it. Our experience thus far would seem to indicate that the large values for the contact angle found by some experimenters must have been due to impurities which prevented the liquid from truly wetting the walls; in such cases a large contact angle is evident even to a superficial observer.

Another question more or less connected with the contact angle is the question as to the effect of the material of the tube. Quincke³ thought that the nature of the material of the tube produced an effect upon the capillary constant, but Volkmann⁴ has disproved these conclusions. Here again, incomplete wetting was probably the cause of the deviations.

Preparation of the Materials.

The benzene used in this work was freed from thiophene by prolonged shaking with several portions of sulfuric acid. It was then washed with water until there was no further test for acid, thoroughly dried over sodium wire, redistilled once, and recrystallized four times (until the

¹ Magie, *Wied. Ann.*, 25, 432 (1885).

² *Z. physik. Chem.*, 12, 452 (1893).

³ *Wied. Ann.*, 61, 267 (1897).

⁴ Volkmann, *Ibid.*, 53, 633 (1894).

freezing point became constant). The benzene was preserved over sodium.¹

The toluene was best "chemically pure" preparation made commercially in Germany. It was treated with concentrated sulfuric acid for a long time, washed with caustic alkali and water, and then shaken up with mercury until the mercury was no longer discolored. Finally it was fractionated (boiling at 110.4° – 110.6° under 768 mm.) and preserved over sodium.

Methyl alcohol was prepared water-free by refluxing first with fresh lime and finally for a long time with metallic calcium. It had a boiling point of 64.65° – 64.75° under 767.5 mm. pressure.

"Absolute" ethyl alcohol, obtained from a trustworthy American firm, and purporting to have only 0.2% of water, was refluxed with metallic calcium for a day, and then redistilled. During the distillation the receiver was well protected from moisture by a tube of freshly ignited lime. The boiling point of the fraction taken was 78.55° at 763.7 mm. The liquid was distilled directly into the surface tension apparatus, with every precaution to exclude moisture. This precaution is essential—a preliminary determination with alcohol which had been exposed to the atmosphere gave a value for the capillary constant appreciably too high.

Our isobutyl alcohol had been carefully fractionated in this laboratory by Dr. H. S. Davis, and had a boiling point of 107.2° – 107.3° , under normal pressure.

Ethyl butyrate was purified by five fractional distillations, and boiled at 120.8° at 756.6 mm.

The water used was all twice distilled, first from alkaline permanganate, and then from a trace of sulfuric acid.

The Execution of the Determinations.

The essential preliminary details having been settled, it was now possible to proceed to develop an apparatus by which the capillary rise of liquids could be accurately measured. The first form which this apparatus took is illustrated in Figs. 1 and 5 (Apparatus III). Except that the narrower tube was very much smaller, the general design was the same as that in Apparatus II (Fig. 3). In Apparatus III the larger tube was 38 mm. in diameter, while that of the smaller was 2.0198 mm. This apparatus was made more compact than No. II, but it still demanded a rather large bulk of liquid (36 cc.), since we dared not soften the glass near the center of the large tube, where the meniscus was to be read. The difficulty was overcome in Apparatus IV (Fig. 6) by sealing into the large tube a closed sinker of glass (partly filled with lead shot), which displaced most of the liquid. The tube above was also filled with a loose plug of glass rod for the same purpose and the total bulk of liquid needed

¹ See Richards and Shipley, *THIS JOURNAL*, 36, 1825 (1915).

was thus reduced to 12 cc. In Apparatus IV the wide tube had the usual diameter of 38 mm. and the capillary tube a diameter of 0.1936 mm., as already stated. The presence of the sinker, with its top very near

but fully below the surface, had the important incidental advantage of much diminishing the slight but irritating vibration which the liquid sometimes suffered in the wide tube. This vibration came chiefly from a distant engine in the Engineering Building of the University, and was especially noticeable when the ground was frozen.

Obviously the first thing to do with each apparatus was to test it by means of some convenient liquid, taking readings at short intervals and in all the four possible positions. Thus any deceptive regions could be detected, and henceforth avoided in the actual use of the apparatus. Each apparatus had a mark etched upon it, for reference as to position.

Apparatus III was the first to be studied in this way. It was carefully cleaned with fresh sulfuric and chromic acid cleaning solution, thoroughly washed with purest water, and filled with water to the desired point. The importance of perfect cleanliness cannot be overemphasized. The apparatus was set in a precisely vertical position with the help of a plumb-line, and after sufficient time had elapsed for the liquid to take the temperature of the thermostat, the meniscus levels

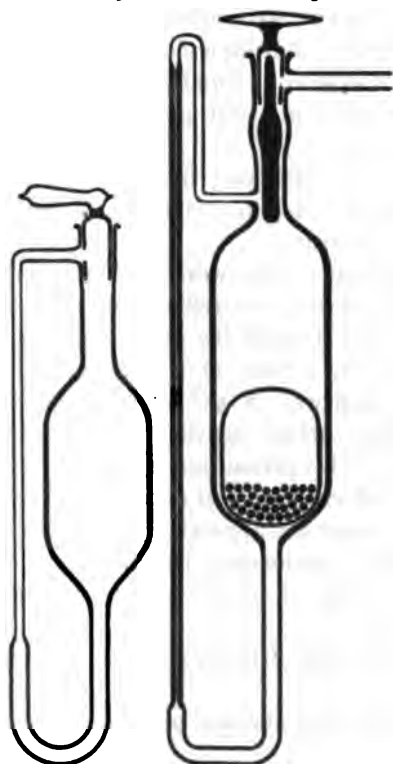


Fig. 5.—Apparatus III in diagrammatic section (about one-third actual size).

Fig. 6.—Apparatus IV in diagrammatic section (about one-third actual size). The loaded sinker is to diminish the necessary volume of liquid.

were carefully read by means of the cathetometer. Then the position of the meniscus in relation to the reference mark was noted, more water put in and new readings taken as before.

At first the readings were not concordant. It was found that the capillary rise was too small when liquid was being added to the large tube. Thus there was a slight lag in the fine tube,¹ probably due to increase

¹ Lord Rayleigh's interesting work on changing surface effects applies only to mixed solutions, such as oleates and saponin. (*Proc. Roy. Soc.*, 47, 281 (1890).)

of the contact angle with a rising thread. Only when the liquid is run rapidly up and down the capillary tube so as to wet thoroughly the walls (of course allowing sufficient time for drainage) are the readings consistent and trustworthy.

A few data may be given to show the importance of this precaution. For example, a preliminary observation with Apparatus III gave an uncorrected (and incorrect) capillary rise of 1.406 cm. On adding 3 cc. of water to the wide tube (a change of level of 2.8 mm.) the capillary rise was only 1.365; and upon adding a little more water the rise was still further diminished to 1.349. On the other hand, when the water in the wide tube was brought back to the original level, the reading was 1.437, which was regularly attained in this way on repetition. This is a total range of six per cent.—an altogether inadmissible irregularity. Hence special precautions must be taken about wetting the capillary before each reading, running the liquid back and forth, and giving plenty of time for drainage. The reading should be approached with a *falling* capillary thread—accomplished by suitably inclining the apparatus for a moment. In this way consistent and satisfactory readings may always be obtained, if the capillary is clean and the liquid pure. One notes that this is precisely the opposite procedure to that necessary in the case of mercury, which must be read in a capillary with a *rising* thread.

The technique having been settled, the calibration of Apparatus III could be undertaken. This was done by making many readings of the height of the water level at frequent intervals and in all the four possible positions. Thus it was found that with this particular apparatus sufficiently concordant results could be obtained only if the liquid level in the wide tube occurred between +0.4 to +1.3 mm. from the mark for all four positions; hence, this limited range was always adhered to. The precaution was important, for a great error may be introduced because of irregularities in the walls of some parts of the tubes. We are inclined to rate this as one of the most serious of the heretofore comparatively unheeded details.

In order to illustrate more fully the method employed, a series of readings in a single setting chosen at random, will be given in full detail. For this reading the apparatus happened to be placed in the thermostat in position *d* (that is, inverted, and viewed from the back, with the larger tube to the left). When the fixed spider-line of the micrometer eyepiece was set on the large meniscus, the reference mark on the smaller tube (2) corresponded to +0.400 on the micrometer scale. The positions of the two meniscuses were then read by measuring in turns of the micrometer the distance of the respective positions from the nearest millimeter as read off from the very carefully graduated scale of the cathetometer. It will be observed that the individual readings varied in maximum less

than 0.01 mm. on each side of the average. This may be taken as about the possible error of a single observation. The mean was doubtless considerably nearer the truth than this.

TWO PARALLEL SERIES OF READINGS: WATER IN APPARATUS III. (20°.)

Position (d) apparatus inverted, back.

Mm. scale.	Micrometer scale settings.							Total reading, mm.
	In turns.						Ave.	
(2) 919.00	+0.458	0.451	0.450	0.457	0.450	0.453	0.376	919.376
(1) 904.00	+1.185	1.183	1.188	1.186	1.186	1.185	0.983	904.983
								14.393
(2) 912.00	+0.461	0.468	0.448	0.459	0.452	0.457	0.376	919.376
(1) 904.00	+1.185	1.189	1.189	1.195	1.197	1.191	0.989	904.989
								14.390
								14.391

Average observed rise, 14.391

This table gives readings only in a single position. In order to be sure that inequalities in the tube caused no error, it was necessary (as already pointed out) to make readings also in the other positions, and the following table contains not only the two averages just given, but six other averages, two for each of the positions (a), (b) and (c), as already defined—*a* being always the position when the tube was erect, with the larger tube to the left.

RESULTS FOR WATER IN APPARATUS III.

Readings in all four positions.

	(a) 1.4378	(b) 1.4416	(c) 1.4389	(d) 1.4393
	1.4379	1.4427	1.4380	1.4390
Av....	(a) 1.4378	(b) 1.4422	(c) 1.4384	(d) 1.4391
	Average of (a) and (b) = 1.4400; average of (c) and (d) = 1.4388			
	Total average..... = 1.4394			

It will be noticed that the readings in any one position are fairly consistent, but that there is considerable variation even in this very carefully selected and elaborately studied tube between the settings in different positions. Position (b) appears to be the most widely deviant, giving the highest results. (d) and (c) agree very closely with each other and with the average. On the whole, therefore, they are to be looked upon as the more accurate. The average of the eight figures has a probable error (according to the theory of least squares) of 0.0004, or 0.03%. Thus, the result is of a degree of accuracy consistent with that of the rest of the problem. Similar deviations were found with other liquids. Usually position (a) gave the lowest results and (b) the highest. Something depends, of course, upon the exact level of the liquid in the tube. With this apparatus determinations of the capillary constant not only of water, as just given, but also of benzene and toluene were made.

Apparatus IV (Fig. 6) (which had a much finer capillary and a sinker occupying most of its bulk, so that less liquid was needed) was calibrated and tested in exactly the same way as Apparatus III. Ethyl alcohol was used for this purpose, because the capillary rise with water was so great in this tube as to take the meniscus out of the range of the small window of optical glass in the thermostat. The results obtained in the various positions are recorded below:

RESULTS FOR ETHYL ALCOHOL IN APPARATUS IV.

Readings in all four positions.

(a) 2.9723	(b) 2.9713	(c) 2.9734	(d) 2.9700
2.9710	2.9713	2.9744	2.9701
2.9704	2.9715	2.9735	2.9702
<hr/>	<hr/>	<hr/>	<hr/>
2.9712	2.9714	2.9738	2.9701
Average of (a) and (b) = 2.9713; average of (c) and (d).....			
Total average.....			=2.9720
			=2.9716

The agreement between the different positions is here much better than in the case of Apparatus III; it leaves nothing to be reasonably desired. The "probable error" is so small as to be negligible.

Benzene was again determined (so as to relate the results of one apparatus with the other). In addition isobutyl and methyl alcohol were likewise studied in this apparatus, as well as ethyl butyrate.

Before any new liquid was introduced, each apparatus was always cleaned with cleaning solution, thoroughly washed with nothing save the best distilled water and finally dried by blowing air dried by phosphorus pentoxide through it for a long time (two to four hours). No grease was used upon the stopcock, which was very finely ground and was moistened with the liquid within. To keep out water and withstand hydrostatic pressure when the apparatus was inverted, the top of the joint of the stopcock was carefully coated with hard paraffin, just before the immersion.

In the two tables which immediately follow there are recorded the successive determinations of the several liquids with Apparatus III and IV. In every case air at atmospheric pressure was present in each of the tubes, with the saturated vapor. Apparatus IV had been arranged so that the air could be removed, but lack of time prevented our making the experiment. The results of Rénard and Guye¹ show, nevertheless, that the effect of the air must be slight.

The tables contain in each case the mean value, obtained by averaging

¹ T. Rénard and P. A. Guye, *J. chim. phys.*, 5, 81-112. Ramsay and Shields's method was employed to measure the rise of liquids in capillary tubes. Measurements were made *in vacuo*, and in the presence of air at atmospheric pressure. The difference between the surface energy in the two cases does not differ by more than 0.5%.

many determinations, in the way already explained in the case of water and benzene.

The tables for the most part explain themselves. The first column names the substance; the second records the observed height (average of at least four averages) of the column between the bottoms of the two menisci; the third gives the correction which must be added to this height on account of the weight of liquid in the capillary meniscus; the fourth gives the sum of the two preceding, or the corrected height; and the fifth gives the density of each substance.

The last two columns perhaps require slightly more detailed description. In the sixth, or the next to the last column of the table is recorded the so-called "capillary constant," usually expressed by the symbol a^2 , which has the dimension of surface, but numerically represents the corrected height in millimeters to which the liquid would rise in a tube of exactly 1 mm. radius. It is calculated according to the equation

$$a^2 = r \times (h + h_m/3),$$

h_m being the height of the meniscus, which is very nearly the radius of the tube in a small tube of this sort.

The last column of the table gives the surface tension computed in terms of dynes per centimeter. These values for surface tension are calculated on the supposition that the angle of contact of liquid in the capillary tube is zero. They can be easily revised in the future provided it is found that this is not the case. The equation used is, of course,

$$\gamma = \frac{1}{2} a^2 (S_1 - S_2) g,$$

the value of g at Cambridge being 980.4, a^2 being expressed in sq. cm., and S_1 and S_2 being the densities of liquid and vapor, respectively.

CAPILLARY CONSTANTS AND SURFACE TENSIONS.

Data obtained with Apparatus III (20.00°), radius of capillary = 1.0099 mm.

Substance.	Average observed height in millimeters.	Correction for small meniscus = $\frac{1}{3} h_m$.	Corrected height in millimeters.	Density 20°/4.	Capillary constant a^2 (in presence of air). (Sq. mm.)	Surface tension dynes per cm.
Water.....	14.394	0.321	14.715	0.9982	14.861	72.62
Benzene.....	6.351	0.311	6.662	0.8788	6.728	28.94
Toluene.....	6.366	0.311	6.677	0.8658	6.743	28.58

Data obtained with Apparatus IV (20.00°), radius of capillary = 0.1936 mm.

Benzene.....	34.620	0.061	34.681	0.8788	6.714	28.88
Methyl alcohol.....	30.063	0.061	30.124	0.7918	5.832	22.61
Ethyl alcohol.....	29.719	0.061	29.780	0.7892	5.765	22.27
Isobutyl alcohol.....	30.016	0.061	30.077	0.8019	5.823	22.85
Ethyl butyrate.....	29.403	0.061	29.464	0.8789	5.704	24.54

Only one pure substance was determined by both tubes, namely, benzene. It will be noticed that the results for benzene are very nearly the

same in both cases, 6.728 and 6.714, the average value for the capillary constant at 20° being 6.721.

This close agreement of the two results with benzene seems to show that there is no essential flaw in the method, and that the radii of the tubes, the correction for each meniscus and the other details have been properly determined.

Our new values for the capillary constant and surface tension of these substances will be seen, on comparing them with the results of others, to be higher than most of the values found by this method already recorded in physico-chemical literature. For example, Quincke¹ found only 14.47 as the capillary constant of water, while Rénard and Guye² found only 6.47 for benzene, instead of 6.72, etc. One of the best of the older results is that of Frankenheim and Sondhauss,³ who found 14.84 for water, a number very near our 14.86; Domke's⁴ more recent result, 14.85, is even better. The carefully obtained results of Walden and Swinne⁵ are doubtless correct relatively to one another, but they all depend upon a value of the capillary constant of benzene which is doubtless too low. Their results would have been much more like ours if they had accepted their own measurement of the diameter of their capillary, and even more consistent with ours if this measurement had been further corrected for the apparently omitted correction for the menisci of the thread of mercury used in calibration. If, as we think, the capillary constant of benzene at 20° is 6.721 instead of the value 6.515 assumed by them,

all their results should be increased by $\left(\frac{6.721}{6.515} - 1\right) = 3.16\%$, and a similar, if not always quite equal, correction should probably be applied to all the results of Ramsay and Shields and Aston, and of Rénard and Guye.

In general it should be noted that higher results obtained by this method are probably to be considered, *à priori*, more accurate than lower ones, because most of the errors in the determination tend to diminish the observed value. If the tube is not perfectly clean, or if the flat surface used for comparison is not large enough, or if the correction for the capillary meniscus is omitted, the observed capillary constant will be too small; and usually at least one of these precautions has not been heeded in the earlier work.

This paper is only a preliminary communication. A large amount of further work upon the subject has already been finished, and more is in prospect. We hope that yet greater accuracy may be attained in the

¹ Quincke, *Pogg. Ann.*, 139, 1 (1870); Brunner's old value (1847) is much better.

² Rénard and Guye, *Loc. cit.* This value for 20° is interpolated from their figures.

³ Frankenheim and Sondhauss, *Pogg. Ann.*, 122, 177 (1864).

⁴ Domke, *Wiss. Abh. d. K. Normal-Aich. Komm.*, III, 1 (1902). He found 14.929 at 18.2°, which would correspond to the above value at 20°.

⁵ *Loc. cit.*

future, bearing in mind the precautions to which attention has been called in this paper.

In conclusion, we are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus employed in this research.

Summary.

In the course of a series of determinations of capillary constants by measuring the capillary rise in fine tubes, the following precautions have been especially emphasized:

First, inequalities in the glass tubes employed were detected and corrected by the use of reversible apparatus.

Secondly, the capillary rise was referred to an unrestricted flat surface 38 mm. in diameter, which is larger than that usually used. It was shown that smaller surfaces are too small and that the insertion of a capillary in the middle of a larger tube causes appreciable error by increasing the capillary effect of the large tube.

Thirdly, special care was taken that the true bottom of the meniscus should be read.

Fourthly, the weight of the fine meniscus was in each case allowed for, and a new approximate formula suggested for its calculation, depending upon the observed height of the meniscus.

Heeding these precautions, determinations of the capillary constants of several important liquids were determined at 20° as follows: water 14.861, benzene 6.721, toluene 6.743, methyl alcohol 5.832, ethyl alcohol 5.765, isobutyl alcohol 5.823, ethyl butyrate 5.704.

CAMBRIDGE, MASS., U. S. A.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE POTENTIAL OF SILVER AGAINST SILVER ION IN CONCENTRATED SOLUTIONS OF POTASSIUM AND OF SODIUM CHLORIDE, AND ITS RELATION TO THE ACTIVITIES OF SUCH SOLUTIONS.

BY GEORGE SHANNON FORBES AND FREDERICK OSBAND ANDEREGG.

Received May 13, 1915.

The present paper records the measurement of the potential of cells of the type $\text{Ag} \mid \text{dilute AgNO}_3 \mid \text{KNO}_3 \mid \text{AgCl in conc. MCl} \mid \text{Ag}$, and an attempt to calculate from the data the activity of chloride ion at high concentrations—a problem of great importance. This work, carried out in the academic year 1912–13, has been left unpublished in the hope of an opportunity to extend the experiments. Because this hope has not yet been fulfilled, the following statement of results is to be regarded, in a sense, as preliminary in character:

Although there exist numerous careful measurements¹ of the potential of silver electrodes against dilute chloride solutions saturated with silver chloride, some of which, as Jahn's, were made to determine concentration of chloride ion, none to our knowledge traverse systematically the field of high concentrations. Nor has anyone investigated solutions unsaturated with silver chloride—a field where results of great interest are obtainable.

Three difficulties are mainly responsible—lack of definiteness in the metallic electrodes, and lack of knowledge of the variation of the solubility product and of the potential at the liquid junction with concentration.

Of the various methods² of preparing electrodes, that suggested by Lewis, to pack pure moist silver oxide into a spiral of platinum wire and then to ignite at 450° (we used an electric oven), proved most satisfactory. Crystalline silver deposits produced on cathodes of platinum foil in silver nitrate served well when carefully prepared. Bell and Feild³ have recently used such electrodes with success. But in all cases electrodes for use in a given cell had to be left short-circuited in silver nitrate solution for days, and then carefully washed before using; otherwise they often showed considerable potentials against each other in any single solution of silver ions. If a cell contains two similar silver electrodes thus equalized, the specific peculiarities of their surface energy should cancel out, and this condition was insured throughout the work. But our experiences would lead us to view with distrust values obtained by opposing any silver electrode to another of different character—a calomel electrode for instance, where the surface energy effect would be uncompensated.

After Nernst,⁴ in 1889, first proposed the principle of the solubility product, Rudolphi⁵ pointed out its tendency to increase with concentration. Stieglitz⁶ pointed out obstacles to applying the law of con-

¹ Nernst, *Z. physik. Chem.*, 4, 155 (1899); Goodwin, *Ibid.*, 13, 641 (1894); Thiele, *Z. anorg. Chem.*, 26, 1 (1900); Jahn, *Z. physik. Chem.*, 33, 545 (1900) and 35, 1 (1900); Sackur, *Ibid.*, 48, 129 (1904); Broensted, *Ibid.*, 50, 481 (1904), and Tolman and Ferguson, *THIS JOURNAL*, 34, 232 (1912). While the proof of this article was being read, there appeared the interesting article by MacInnes and Parker, *Ibid.*, 37, 1445 (1915), on potassium chloride concentration cells, ingeniously contrived to avoid transference, including solutions as concentrated as half normal. While opportunity for extended comment is lacking, it may be noted that the abnormally low "activities" of the ions in the solutions investigated by them are continued in still more striking fashion at higher concentrations as measured by us.

² See 1, also Richards and Lewis, *Z. physik. Chem.*, 28, 1 (1899); Lewis, *THIS JOURNAL*, 28, 166 (1906); Bell and Feild, *Ibid.*, 35, 715 (1913); Gibbons and Getman, *Ibid.*, 36, 1630 (1914); Jones, *Ibid.*, 37, 756 (1915).

³ Nernst, *Z. physik. Chem.*, 4, 372 (1889).

⁴ Rudolphi, *Ibid.*, 17, 385 (1895).

⁵ Stieglitz, *THIS JOURNAL*, 30, 946 (1908).

centration effect, but considered it a good empirical approximation due to compensation of opposing errors. Washburn¹ has apparently derived a sound theoretical basis for treatment of the solubility product from the original viewpoint, but the solutions must be "sufficiently dilute." Noyes² and his associates have shown the variations in the solubility product to increase with the solubility and valences of a salt. According to this conclusion, the product should be more constant in the case of silver chloride than with almost any other salt. The danger of assuming constancy is fully realized, but our results must show at least the effect of superposing changes in activities and in solubility product at different concentrations. As for the most probable value of solubility product times 10^{10} at 25° , omitting Hollemann's³ early work, Kohlrausch and Rose⁴ give 2.13; Goodwin's⁵ value, 1.56, is raised to 1.73 if $F = 96,540$ and viscosity corrections are made; Thiele⁶ obtains 2.00; Kohlrausch⁷ later finds 1.75; from measurements of Melcher⁸ we calculate 1.93; Böttger⁹ upholds 1.99; and finally, Glowczynski,¹⁰ titrating the silver chloride in solution at 25° with NH_4CNS , finds 1.44. He believes that previous investigators have had impure AgCl , but as his original paper is not accessible, his very low value is not for the present taken instead of the above array of concordant data. The average of the six accepted determinations is 1.92×10^{-10} .

Potassium and sodium chlorides were purified by precipitation from water solution of hydrochloric acid gas made by heating the pure concentrated acid. The precipitates were washed, dried, ignited, and dissolved in redistilled water almost to saturation. These solutions were also saturated with precipitated silver chloride. On dilution with a known volume of water, a precipitate appeared, and the solution, after settling, was still saturated with silver chloride. Concentrations of alkali chloride were calculated from analyses, those of silver chloride by interpolation on a large curve drawn from data obtained by one of us.¹¹ Solutions unsaturated with silver chloride, but containing it in constant concentration, were also used. To prepare these, equal volumes of alkali chloride and of water were treated with a volume of silver nitrate

¹ Washburn, *THIS JOURNAL*, 32, 467, 653 (1910).

² Noyes and Associates, *Ibid.*, 33, 1643, 1650, 1663, 1673, 1807, 1827, 1836 (1911).

³ Holleman, *Z. physik. Chem.*, 12, 132 (1893).

⁴ Kohlrausch and Rose, *Ibid.*, 12, 242 (1893).

⁵ Goodwin, *Ibid.*, 13, 641 (1894).

⁶ Thiele, *Z. anorg. Chem.*, 24, 57 (1900).

⁷ Kohlrausch, *Z. physik. Chem.*, 64, 129 (1908).

⁸ Melcher, *THIS JOURNAL*, 32, 50 (1910).

⁹ Böttger, *Z. physik. Chem.*, 56, 83 (1906).

¹⁰ Glowczynski, *C. A.*, 1915, 741.

¹¹ Forbes, *THIS JOURNAL*, 33, 1937 (1911).

identical in both cases, and on mixing known amounts of the products, solutions constant in silver content were obtained, until precipitation occurred.

Solutions of 0.01 *N* silver nitrate and of alkali chloride containing silver chloride were contained in separate wide-mouthed bottles immersed in a thermostat kept at 25.0°. As a precipitate would form on mixing, the junction could not be made and calculated in the manner usually applied to concentration cells with transference. Siphons of pure concentrated potassium nitrate in agar-agar were, therefore, used to connect the solutions. Sackur¹ has found the electromotive force of such cells independent of the concentration of the nitrate. Our chloride solutions were much more concentrated than his, but as the mobilities of all the ions involved (except sodium) were very nearly equal, the error introduced by junctions at the boundaries of the concentrated potassium nitrate solutions should be inconsiderable.

The possibility of variable oxidation of the electrodes by dissolved air was tested by measuring the potentials of given cells in air, in pure nitrogen from an apparatus used in atomic weight investigation, and in carbon dioxide. As the only variations were traced to the stirring of the solutions by bubbles, subsequent measurements were made in air.

Stirring the chloride solutions greatly disturbed the potential of the cells. Tolman² has reviewed the hypotheses made to account for such effects, and has advanced a plausible one of his own. Kistiakowsky³ holds that stirring is necessary, in the case of solid electrodes, to submerge the slight differences in potential between different points on the same electrode. This would be particularly true of metals in which a gas film tended to form. The disturbances noted by us increased with the speed of stirring, and failed to approach limiting values with any speed that we could attain. Therefore, the solutions, after brisk stirring, were allowed to stand at rest until the potential assumed a value constant for hours within a few tenths of a millivolt.

The total potential of each cell was measured to one-tenth millivolt, without interpolation, by the compensation method. The potentiometer was calibrated, and the corrections applied. The standard cadmium cell was carefully made up, and checked at intervals against cells kindly loaned by other investigators.

Tables I and II exhibit data and results of calculations for solutions saturated with silver chloride. Concentrations are expressed in mols per liter and in mol fractions. As each molecule of silver chloride combines with two of alkali chloride up to 1.5 *N*, and with three above 1.5

¹ Sackur, *Z. physik. Chem.*, 48, 129 (1904).

² Tolman, *THIS JOURNAL*, 33, 1836 (1911); 36, 466 (1914).

³ Kistiakowsky, *Z. Elektrochem.*, 14, 113 (1908).

TABLE I.—POTASSIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART I.

$[\text{KCl}]$, Mols/Liter.	Density, 25°/4°.	$[\text{KCl}] \times 10^4$, Mol Fraction.	Total $[\text{Ag}] \times 10^4$, Mols/Liter.	Total $[\text{Ag}] \times 10^4$, Mol Fraction.	$[\text{KCl}] - [\text{Ag}] \times m$, Mols/Liter.	$[\text{KCl}] - [\text{Ag}] \times m \times 10^4$, Mol Fraction.	Potential Found, $[\text{Ag}^+] = 0.009314$.
3.917	1.1657	7.476	6.185	1.179	3.898	7.441	0.4759
3.926	1.1674	7.482	6.245	1.189	3.907	7.446	0.4752
3.797	1.1610	7.428	5.722	1.089	3.780	7.395	0.4753
3.890	1.1661	7.395	6.024	1.145	3.872	7.361	0.4737
3.154	1.1340	5.837	2.644	0.4967	3.146	5.822	0.4668
2.677	1.1131	4.990	1.493	0.2807	2.672	4.982	0.4590
2.508	1.1061	4.679	1.198	0.2234	2.504	4.672	0.4586
1.976	1.0833	3.663	0.601	0.1113	1.974	3.660	0.4526
1.952	1.0819	3.619	0.580	0.1073	1.950	3.616	0.4518
1.820	1.0791	3.353	0.467	0.0860	1.819	3.350	0.4453
1.648	1.0690	3.147	0.352	0.0650	1.647	3.145	0.4446
1.383	1.0526	2.556	0.219	0.0405	1.383	2.556	0.4413
0.977	1.0496	1.767	0.121	0.0219	0.977	1.767	0.4328
0.853	1.0402	1.545			0.853	1.545	0.4296
0.758	1.0357	1.374			0.758	1.374	0.4269
0.381	1.0193	0.686			0.381	0.686	0.4145

TABLE I.—POTASSIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART II.

$[\text{KCl}]$, Mols/Liter.	Potential calc., $[\text{Ag}^+] = 1.000$.	$[\text{Ag}^+] \times 10^4$, Gram Ion/Liter.	$[\text{Ag}^+] \times 10^4$, Mol Fraction.	$\frac{A}{150.6}$	$\frac{A}{150} \times \frac{v}{\%}$	$\frac{1.92 \times 10^{-10}}{[\text{Ag}^+][\text{KCl}]} \text{ corr.}$	$\frac{1.92 \times 10^{-10}}{[\text{Ag}^+][\text{KCl}]} + \frac{A_v}{150.6}$	$\frac{1.92 \times 10^{-10}}{[\text{Ag}^+][\text{KCl}]} + \frac{A}{150.6}$
3.917	0.5960	0.834	1.59	0.634	0.637	0.591	0.927	0.932
3.926	0.5953	0.854	1.62	0.634	0.637	0.575	0.903	0.907
3.797	0.5954	0.857	1.63	0.636	0.639	0.593	0.928	0.932
3.890	0.5938	0.909	1.73	0.635	0.637	0.546	0.856	0.860
3.154	0.5869	1.187	2.23	0.649	0.652	0.514	0.789	0.793
2.677	0.5791	1.610	3.03	0.660	0.663	0.446	0.673	0.676
2.508	0.5787	1.636	3.05	0.664	0.667	0.469	0.705	0.708
1.976	0.5727	2.067	3.83	0.684	0.682	0.471	0.690	0.688
1.952	0.5719	2.130	3.95	0.685	0.683	0.462	0.677	0.674
1.820	0.5654	2.739	5.05	0.691	0.689	0.385	0.559	0.557
1.648	0.5647	2.820	5.20	0.700	0.697	0.413	0.593	0.592
1.383	0.5614	3.211	5.93	0.717	0.713	0.432	0.607	0.603
0.977	0.5529	4.461	7.92	0.751	0.745	0.441	0.591	0.588
0.853	0.5497	5.065	9.18	0.759	0.753	0.444	0.590	0.586
0.758	0.5470	5.616	10.18	0.767	0.761	0.451	0.593	0.587
0.381	0.5346	9.112	16.55	0.801	0.796	0.553	0.695	0.692

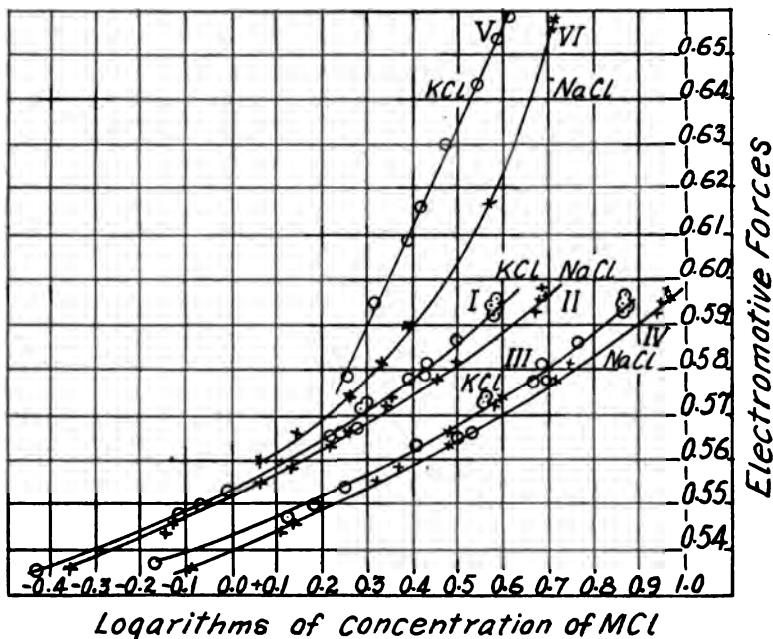
TABLE II.—SODIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART I.

[NaCl], Mols./Liter.	Density, 25°/4°.	[NaCl] X 10 ³ , Mol Fraction.	Total [Ag] X 10 ³ , Mols./Liter.	Total [Ag] X 10 ⁴ , Mol Fraction.	[NaCl] — [Ag] X m, Mols./Liter.	[NaCl] — [Ag] X m X 10 ³ , Mol Fraction.	Potential Found, [Ag] ⁺ = 0.009314.
5.013	1.1841	9.196	5.936	1.0890	4.895	9.163	0.4776
4.992	1.1837	9.152	5.925	1.0860	4.974	9.119	0.4768
4.895	1.1802	8.975	5.510	1.0100	4.878	8.945	0.4758
4.781	1.1758	8.761	5.085	0.9318	4.766	8.733	0.4736
3.080	1.1123	5.613	1.297	0.2364	3.076	5.606	0.4611
2.815	1.1025	5.114	0.988	0.1817	2.812	5.108	0.4586
2.171	1.0761	3.954	0.500	0.0907	2.169	3.951	0.4537
2.121	1.0680	3.877	0.470	0.0861	2.119	3.884	0.4517
1.700	1.0603	3.086	0.280	0.0508	1.699	3.084	0.4451
1.640	1.0579	2.978	0.257	0.0467	1.639	2.977	0.4432
1.393	1.0486	2.517	0.174	0.0316	1.393	2.517	0.4404
1.300	1.0450	2.358	0.159	0.0288	1.300	2.358	0.4379
1.154	1.0390	2.094	0.121	0.0220	1.154	2.094	0.4350
0.758	1.0247	1.376			0.758	1.376	0.4264
0.719	1.0232	1.301			0.719	1.301	0.4260
0.441	1.0126	0.798			0.441	0.798	0.4147

TABLE II.—SODIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART II.

[NaCl], Mols./Liter.	Potential calc., [Ag] ⁺ = 1.000.	[Ag ⁺] X 10 ⁴ , Gram Ion/Liter.	[Ag ⁺] X 10 ⁻¹¹ , Mol Fraction.	$\frac{A}{127.0}$	$\frac{A}{125.0} \times \frac{\gamma}{\gamma_0}$	$\frac{1.92 \times 10^{-10}}{[Ag^+][NaCl]} \text{ corr.}$	$\frac{1.92 \times 10^{-10}}{[Ag^+][NaCl]} + \frac{A\gamma}{125 \gamma_0}$	$\frac{1.92 \times 10^{-10}}{[Ag^+][NaCl]} + \frac{A}{127}$
5.013	0.5977	0.780	1.43	0.396	0.684	0.493	0.720	1.242
4.992	0.5969	0.805	1.47	0.397	0.685	0.479	0.700	1.204
4.895	0.5959	0.837	1.53	0.401	0.686	0.470	0.685	1.173
4.781	0.5937	0.911	1.67	0.406	0.686	0.442	0.645	1.088
3.080	0.5812	1.482	2.70	0.499	0.695	0.422	0.607	0.845
2.815	0.5787	1.634	2.97	0.516	0.698	0.418	0.599	0.813
2.171	0.5738	1.977	3.60	0.566	0.713	0.448	0.627	0.792
2.121	0.5718	2.138	3.91	0.568	0.714	0.424	0.594	0.746
1.700	0.5652	2.775	5.04	0.599	0.717	0.407	0.568	0.680
1.640	0.5633	2.976	5.40	0.609	0.724	0.394	0.544	0.647
1.393	0.5605	3.320	6.02	0.632	0.734	0.415	0.566	0.657
1.300	0.5580	3.660	6.64	0.642	0.737	0.404	0.548	0.630
1.154	0.5551	4.096	7.43	0.659	0.746	0.406	0.544	0.616
0.758	0.5465	5.727	10.38	0.710	0.772	0.442	0.573	0.623
0.719	0.5461	5.816	10.52	0.713	0.774	0.459	0.593	0.644
0.441	0.5438	9.032	16.31	0.756	0.800	0.482	0.603	0.636

N ,¹ the silver concentration must be multiplied by two, or three, and subtracted from that of the alkali chloride in each case. Observed potentials are given, also those calculated for cells containing normal silver ion by adding $0.05913 \log 1.000/0.009314$, or 0.1201 volt, to observed values, where the dissociation of $0.01 N$ silver nitrate is taken as 93.14% at 25° . Curves I, II exhibit the latter potentials plotted against \log mols/liter, and II, IV the same plotted against \log mol fractions $\times 10^2$.



All these solutions were saturated with silver chloride. Next in order are tabulated silver ion concentrations calculated from the formula $\log [Ag^+] = \log 0.009314 - \pi/0.05913$. The error is 4% per millivolt in all cases. Degree of dissociation is calculated in two ways, first as Λ_s/Λ_∞ , using 150.6 and 127.0 , the customary values, respectively, of Λ_∞ at 25° ; second by extrapolating Λ to infinite dilution by the method of Kraus and Bray,² we found 150.0 for potassium chloride, and 125.0 for sodium chloride, and multiplied the conductance ratio by the ratio of the viscosities³ rather than by any power of the same. In the case of the potassium chloride, reliable data⁴ for viscosities were found and

¹ Forbes, *THIS JOURNAL*, **33**, 1937 (1911).

² Kraus and Bray, *Ibid.*, **35**, 1315 (1913).

³ See Sutherland, *Phil. Mag.*, **3**, 161 (1902); Bousfield, *Z. physik. Chem.*, **53**, 257 (1905); Washburn, *THIS JOURNAL*, **33**, 1469 (1911).

⁴ Wagner, *Z. physik. Chem.*, **5**, 31 (1890); Reyer, *Ibid.*, **2**, 744 (1888); Brueckner, *Ann. physik.*, **42**, 294 (1891); Hoskings, *Phil. Mag.*, [6] **17**, 502 (1909). Hosking's

applied up to 2.0 *N* only. Data for viscosity and degree of dissociation were interpolated on smoothed curves drawn on a large scale. Because of the length of the process for calculating the corrected values, these are given below without comment. By dividing 1.92×10^{-10} by $[\text{Ag}^+]$ we obtain the apparent effective concentration or activity of the chloride ion, and by dividing also by $[\text{MCl}]$ corrected for complex formation, we obtain a new set of figures for effective degree of dissociation. The succeeding column gives the ratio between these figures and the corrected degree of dissociation. It will be noted that the activity of the chloride ion in relation to concentration decreases as concentration increases from small values up to 1.7 *N*, and the minima attained—0.385 and 0.394 are almost identical for both chlorides. These minima are not to be attributed to any decrease in the solubility product of silver chloride as concentration increases, for Noyes¹ has shown the product to increase. Nor can the decreases be mainly due to absence of correction for the liquid junctions, because the decrease is smaller in the case of sodium chloride, where the difference in ionic mobilities is far more pronounced than in potassium chloride. In passing through the concentration, 1.7, the formula of the complex changes from M_2AgCl_3 to M_3AgCl_4 ,² showing this region to be worthy of careful study. As the concentration is increased beyond this point the change in the nature of the medium seems to prevail over the tendencies which have acted to lower the relative activity of the chloride ion. A sharp rise in the ratio of activity to concentration takes place as higher concentrations are approached, which is much more pronounced in the case of potassium chloride, corresponding to the greater power of this salt to dissolve AgCl .

In the last column we have the ratio between the effective degree of dissociation, calculated from the solubility product, and the degree of dissociation calculated in the usual simple fashion. With potassium chloride the values follow the same trend as in the column before, but with sodium a huge increase is noted at high concentrations, imputing to the solution an activity 24% greater than could be explained by complete dissociation. The viscosity correction appears, therefore, to yield more reasonable figures in calculating dissociation from conductivity.

Measurements were also made in solutions where the concentration of the alkali chloride was varied, as described above, without changing that of the total dissolved silver, at least when expressed in mols per liter. Curve V in the graph shows the results in potassium chloride, and values were interpolated between 20° and 30°, while Brueckner's were extrapolated from 15° and 20° to 25°.

¹ Noyes and associates, *THIS JOURNAL*, 33, 1643, 1650, 1663, 1673, 1807, 1827, 1836 (1911).

² Forbes, *Ibid.*, 33, 1937 (1911).

TABLE III.—CONSTANT [AgCl], VARIABLE [KCl].

[MCl] Mols/Liter.	Potential found, [Ag ⁺] = 0.009314.	Potential calc., [Ag ⁺] = 1.000.	[Ag ⁺] × 10 ⁴ , Mols/Liter.	$\frac{\Delta}{\Delta c}$.	[Cl ⁻].	[Ag ⁺] [Cl ⁻] ³ × 10 ¹⁰ .	[Ag ⁺] [Cl ⁻] ³ × 10 ¹⁰ .
4.064	0.5385	0.6586	0.0736	0.632	2.563	3.17	..
3.474	0.5225	0.6426	0.1357	0.641	2.222	3.34	..
2.968	0.5100	0.6301	0.2209	0.650	1.395	3.06	..
2.624	0.4957	0.6158	0.3565	0.658	1.727	3.17	..
2.476	0.4890	0.6091	0.500	0.663	1.642	3.63	..
2.055	0.4738	0.5939	0.904	0.679	1.395	3.43	..
1.824	0.4591	0.5792	1.603	0.689	1.257	4.00	..

TABLE IV.—CONSTANT [AgCl], VARIABLE [NaCl].

5.143	0.5378	0.6579	0.0748	0.389	2.000	1.20	..
5.080	0.5357	0.6558	0.0812	0.392	1.991	1.28	..
3.690	0.4968	0.6169	0.1868	0.463	1.708	1.59	..
3.262	0.4875	0.6076	0.3410	0.488	1.592	2.19	..
2.504	0.4705	0.5906	1.028	0.539	1.350	3.41	..
2.454	0.4694	0.5895	1.098	0.543	1.332	3.46	..
2.159	0.4617	0.5818	1.448	0.565	1.220	3.21	..
1.808	0.4540	0.5741	1.955	0.592	1.070	2.57	..
1.394	0.4458	0.5659	2.690	0.632	0.881	..	1.46
1.180	0.4405	0.5606	3.307	0.656	0.774	..	1.53
0.943	0.4348	0.5549	4.128	0.685	0.646	..	1.11

Curve VI those in sodium chloride, plotting potentials calculated as against normal silver ions against concentrations in mols per liter only, as the mol fraction curves would cut Curves I and II in a confusing fashion. In the potassium chloride (Table III) total silver was 1.43×10^{-4} , and in the sodium chloride (Table IV) 3.73×10^{-5} mol/liter. The constants in the last column are derived as follows, using the unmodified Law of Concentration Effect for this first approximation:

$$[\text{Ag}^+] [\text{Cl}^-] = k_1 [\text{AgCl}]$$

$$[\text{AgCl}] [\text{Cl}^-]^n = k_2 [\text{AgCl}_n^{n+1}]$$

Eliminating (AgCl) between the equations,

$$\frac{[\text{Ag}^+] [\text{Cl}^-]}{k_1} = \frac{k_2 [\text{AgCl}_n^{n+1}]}{[\text{Cl}^-]^n}$$

But as the total silver is constant, and almost equal to (AgCl_n^{n+1}) , as practically all the silver is in the form of the complex ion, we have

$$[\text{Ag}^+] [\text{Cl}^-]^{n+1} = K_n$$

The complex ion existing above 1.7 N has been found by one of us¹ to be AgCl_4^{4-} , whence $n = 3$. The degree of dissociation is taken as

¹ Forbes, THIS JOURNAL, 33, 1937 (1911).

Λ/Λ_{∞} . If the values corrected for viscosity were used, the results for potassium chloride would be little changed, but no approach to a constant could be obtained in the case of sodium chloride. This work with constant silver concentration was interrupted when barely begun, but it promises to be of much interest, as also determinations in which chloride concentration is kept constant, but total silver is varied, which would help greatly in the interpretation. No conclusion can at present be drawn as to the significance of the difference in shape, slope, or position of the two curves given.

Summary.

The activity of chloride ion in concentrated solutions of sodium and of potassium chloride saturated with silver chloride is calculated from potential measurements, using silver electrodes, and a junction of concentrated potassium nitrate, to eliminate diffusion potentials. The solubility product, for want of a better hypothesis, is assumed constant, and evidence is offered to show that its variations do not greatly affect the conclusions.

The values obtained by this method are always smaller than those calculated from conductivities except in the most concentrated solutions of sodium chloride. The dissociation calculated from them reaches a minimum at 1.7 *N*.

Solutions variable in alkali chloride, but constant in silver chloride, afford results supporting the hypothesis that the complex K_2AgCl_4 exists in concentrations above 1.7 *N*.

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EQUILIBRIUM IN THE SYSTEM DISODIUM HYDROGEN ARSENATE, LEAD NITRATE, AND WATER AT 25° C.

BY B. E. CURRY AND T. O. SMITH.

Received April 30, 1915.

In the course of an investigation of commercial lead arsenates the writers experienced the need of more definite information than the literature affords concerning the theoretical compounds of lead and arsenic acid. The compounds reported by previous workers have evidently been formed under ordinary synthetic rather than equilibrium conditions. The methods of preparation in most cases have apparently been selected with the view of duplicating those used by the manufacturer.

The most important source of arsenic used in the preparation of commercial lead arsenate is disodium hydrogen arsenate. This is the cheapest source of arsenic in suitable form. The lead salts used are the nitrate and the acetate. The nitrate is given the preference because it is the cheaper salt on the basis of lead content; also, because the product formed from the nitrate under manufacturing conditions possesses more desirable physical

properties and has a higher arsenic content. For practical purposes the data secured from an equilibrium study would be most valuable if these salts were taken.

The composition of most brands of commercial lead arsenate is very near that of lead hydrogen arsenate. They contain, in general, more lead and less arsenic than the theoretical salt and are said to be mixed with the triplumbic arsenate in varying amounts, depending upon the method and conditions of manufacture.

Lead hydrogen arsenate, PbHAsO_4 , contains theoretically 64.28% PbO ; 33.13% As_2O_5 and 2.59% H_2O . Triplumbic arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, contains theoretically 74.42% PbO and 25.58% As_2O_5 .

The thermostat used in this work was maintained at $25^\circ \pm 0.2^\circ$. The rotating shaft was equipped to carry the bottles with their length in the plane of rotation, so that the contents of the bottle by breaking on its ends were thoroughly shaken. The salts were pure disodium hydrogen arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and pure lead nitrate, $\text{Pb}(\text{NO}_3)_2$. For convenience in making up the bottles, standard solutions were prepared and the required amount of each measured from a buret. The percentages were computed so that their combined weight was 2 g. in each bottle. The bottles, 500 cc. in volume, were weighed and, after the standard solutions had been measured into them, water was added to make the total contents 450 g., as shown in the following table:

TABLE I.

Bottle.	% As_2O_5 .	G. As_2O_5 .	% PbO .	G. PbO .	Total g. salts.	Total g. contents.
1.....	5	0.10	95	1.90	2.00	450
2.....	10	0.20	90	1.80	2.00	450
3.....	20	0.40	80	1.60	2.00	450
4.....	25	0.50	75	1.50	2.00	450
5.....	26	0.52	74	1.48	2.00	450
6.....	27	0.54	73	1.46	2.00	450
7.....	28	0.56	72	1.44	2.00	450
8.....	29	0.58	71	1.42	2.00	450
9.....	30	0.60	70	1.40	2.00	450
10.....	31	0.62	69	1.38	2.00	450
11.....	32	0.64	68	1.37	2.00	450
12.....	33	0.66	67	1.34	2.00	450
13.....	34	0.68	66	1.32	2.00	450
14.....	35	0.70	65	1.30	2.00	450
15.....	37	0.74	63	1.26	2.00	450
16.....	40	0.80	60	1.20	2.00	450

The bottles were allowed to remain in the thermostat three months. Doubtless equilibrium was reached in a much shorter time. They were then taken from the rotating shaft and allowed to stand in the thermostat until the solid phase had separated out. The supernatant liquid was then filtered off, the solid phase being left in the bottles. The arsenic oxide

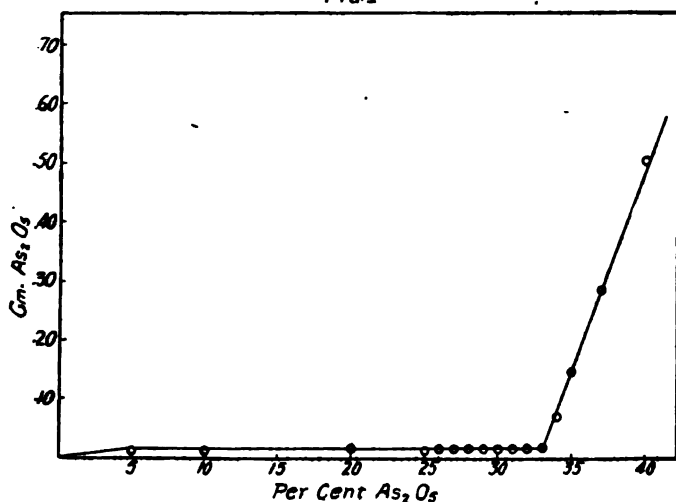
was determined in 100 cc. portions of the filtrates by the usual iodine method. The data are given in Table II.

TABLE II.

Bottle.	% As_2O_5	G. As_2O_5 in 100 cc. filtrate.	Bottle.	% As_2O_5	G. As_2O_5 in 100 cc. filtrate.
1.....	5	0.0086	9.....	30	0.0144
2.....	10	0.0115	10.....	31	0.0144
3.....	20	0.0153	11.....	32	0.0144
4.....	25	0.0115	12.....	33	0.0173
5.....	26	0.0144	13.....	34	0.0690
6.....	27	0.0144	14.....	35	0.1495
7.....	28	0.0144	15.....	37	0.2875
8.....	29	0.0144	16.....	40	0.5060

The above data are plotted in Fig. 1, using as ordinates the weight in grams of As_2O_5 in 100 cc. of the filtrate as abscissae the percentage of As_2O_5 in the combined weight of the reacting compounds.

FIG. 1



The above data show that a compound is formed at about 33%, which is the As_2O_5 content of lead hydrogen arsenate. They also show that only one compound is formed, unless the solubilities are so nearly equal as not to be detected by a change in the curve. In order to show that other compounds do not exist in an equilibrium of these salts at the given temperature, an analysis was made of the solid phase in several of the bottles. To procure the sample for analysis the bottle was taken from the thermostat and the solid phase was poured upon a suction filter by aid of the mother liquor remaining with it. The mother liquor was removed as completely as possible by strong suction. The solid was dried and the lead determined by the usual method of weighing the sulfate. Table III gives the results.

TABLE III.

Bottle.	% PbO found.	Variation from theoretical PbO content of lead hydrogen arsenate.
3.....	65.49	+1.21%
5.....	64.45	+0.17%
8.....	64.66	+0.38%
12.....	64.44	+0.16%

Conclusion.—In the system disodium hydrogen arsenate, lead nitrate and water there exists at 25° only one compound, lead hydrogen arsenate.

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THE SOLUBILITY CURVES OF SALT HYDRATES: CALCIUM NITRATE.

By HUGH STOTT TAYLOR AND WILLIAM NOLAND HENDERSON.

Received April 20, 1915.

Systems formed of two components have attracted considerable attention from phase rule investigators. The phase relationships of systems composed of mixtures of salts and water have been the chief object of experimental study. They may broadly be classified according as the components separate from solution in the pure state or as combination occurs between them with the formation of definite compounds. To the latter class belong the salt hydrates. They form a class of extreme importance, owing to their frequent occurrence in the field of inorganic chemistry. Study of such systems leads to a subdivision of hydrates into two classes, those possessing a definite melting point forming a liquid phase of the same composition as the solid hydrate and those which do not so behave.

Of the latter class of crystalline hydrates, which show no true melting point, but on the other hand a transition point, the classical example is sodium sulfate decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Below 32.4° the saturated solution exists in stable equilibrium with the salt hydrate. Above that temperature, solutions are in stable equilibrium with the anhydrous salt and the solubility curve shows a sharp break at the transition temperature. At this temperature partial fusion occurs, during which the temperature remains constant. This is no true melting point, however, for the composition of the liquid phase is not the same as that of the original solid. The system also shows unstable solubility curves. For example, the curves of the decahydrate and the anhydrous salt may be continued some distance into the unstable region. That of the anhydrous salt, if sufficiently prolonged, meets the solubility curve of the unstable heptahydrate, which exists in equilibrium with solutions of higher concentrations than

those in equilibrium with the decahydrate at the same temperature. This phenomenon is characteristic. The solid phase which is stable at the given temperature has the least solubility at that temperature.

The hydrates of ferric chloride¹ illustrate effectively the case of hydrates possessing definite melting points. A succession of hydrates with 12, 7, 5 and 4 molecules of water possess definite melting points corresponding to the point of maximum solubility, in composition the same as that of the solid hydrate, at 37°, 32.5°, 56° and 73.5°, respectively, and solubility curves with retroflex portions. Definite transition temperatures exist at 27.4°, 30°, 55° and 66°, at which the stable existence of the next lower hydrate begins, the solubility curves showing change of direction. The solubility curves may be prolonged into the unstable regions.

The case of calcium chloride hydrates² illustrates another point in the study of such hydrates. The highest hydrate of calcium chloride, the hexahydrate, shows a definite melting point similar to those of the ferric chloride hydrates at 30.2°, and also a retroflex portion of the curve. As, however, at a temperature of 29.8° the tetrahydrate, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, becomes the stable solid phase in equilibrium, it is obvious that the solubility curve of the hexahydrate above this temperature represents metastable equilibrium and the melting point of the hexahydrate is a metastable melting point due to suspended transformation.

It will be seen, therefore, that true melting points may be met with both in the stable and unstable regions. Now certain hydrates have been found existing in two or more crystalline modifications, the one stable, the other unstable, over a given range of temperatures. The tetrahydrate of calcium chloride shows too such modifications, an α - and a β -form, the former stable, the latter always unstable. Neither of these forms shows a melting point, since they pass through a transition point to the next lower hydrate before the melting point is attained. It is conceivable, however, that hydrates should exist in two crystalline forms each possessing a definite melting point. In two-component systems other than salt hydrates such cases are known. Two such cases may here be cited. The system iodine-chlorine³ forms a compound ICl , existing in two crystalline modifications each possessing a definite melting point. Further, as has been shown by Philip,⁴ phenol can combine with *p*-toluidine, forming an equimolecular compound existing in two crystalline forms melting at 28.5° and 30°, respectively.

Recent investigations of the two-component system calcium nitrate-water have tended to show that this phenomenon may also be established

¹ Roozeboom, *Z. physik. Chem.*, 10, 477 (1892).

² Roozeboom, *Ibid.*, 4, 31 (1889).

³ Stortenbeker, *Ibid.*, 3, 11 (1889).

⁴ *J. Chem. Soc.*, 83, 821 (1903).

in the case of salt hydrates. The phase relationships at various temperatures from -28° to 151° were investigated by one of the authors under the direction of Bassett, whereby it was shown¹ that in addition to ice and the anhydrous salt, three hydrates could exist in stable equilibrium with the saturated solutions, *viz.*, with 4, 3, and 2 molecules of water. The first two hydrates showed true melting points at 42.7° and 51.1° , respectively, the last a transition point. Later it was shown by Hasselblatt,² in investigations of the velocity of crystallization, that cadmium nitrate tetrahydrate cannot be inoculated with calcium nitrate tetrahydrate, but that the cadmium salt readily inoculates the melted calcium salt. It was therefore concluded that two forms of the tetrahydrate of calcium nitrate exist, the unstable form isomorphous with the tetrahydrate of cadmium nitrate. The melting points of the two forms were determined, and gave 42.6° and 39.7° , the former in agreement with the value of Bassett and Taylor. Obviously, therefore, to the phase diagram previously established there could be added the solubility curve of unstable calcium nitrate tetrahydrate. This should show a maximum solubility corresponding to the composition of the solid phase at the temperature of 39.7° , the melting point of the substance as well as a retroflex portion of the curve. To establish these points the experimental investigation of the solubility curve has been undertaken.

Immediately subsequent to the publication by Bassett and Taylor of the results of the investigation of the two-component system calcium nitrate-water, there appeared a communication by D'Ans³ on the solubility isothermals of the alkali-earth nitrates in alcohol-water mixtures. It was shown, *inter alia*, that calcium nitrate existed at 25° , in stable equilibrium with the various solutions as tetrahydrate, anhydrous salt and alcoholate, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$. It is remarkable that neither of the two lower hydrates were discovered, as it is generally found that the dehydrating action of the alcohol passes successively through the stages of hydrates found in the two-component system. Further, the metastable solubilities of the anhydrous salt in various alcohol-water mixtures and in pure water were given. For the latter a value of 82.5 g. $\text{Ca}(\text{NO}_3)_2$ per 100 g. solution was given. The work of Bassett and Taylor had shown that between 50° and 151° the boiling point of the saturated solution, the solubility curve of the anhydrous salt ran practically parallel to the axis of temperature and that at the highest temperature the solubility amounted to 79.0 g. per 100 g. solution. If the figure of D'Ans be correct the curve of the anhydrous salt in the unstable region must show a very sharp change of direction below 50° , or in other words the heat of solution in the almost

¹ *J. Chem. Soc.*, 101, 576 (1912).

² *Z. physik. Chem.*, 83, 1 (1913).

³ *Ibid.*, 82, 35 (1913).

saturated solution must undergo a very sudden change in the region 25–50°, which seems, however, little likely. To test this point, a determination of the solubility of the anhydrous salt at 25°, was made.

Experimental.

The saturated solutions analyzed in the experiments on the unstable tetrahydrate solubility curve were all prepared from supersaturated solutions from which all germs of the stable hydrate were removed by maintenance at a temperature of 50–60°, for a period of time. Crystallization was induced in the solutions by inoculation with a small crystal of cadmium nitrate tetrahydrate and the solution allowed to come into equilibrium with the solid phase by standing in the thermostat at the desired temperature, which could be controlled to 0.05°. This procedure was adopted owing to the instability of the β -tetrahydrate and the readiness with which it changed to the α -form when attempt was made to isolate it. In all cases separate concordant determination of the various points were obtained.

From the temperature of 30° upwards the attainment of equilibrium was comparatively easy and reproducible figures readily obtainable. Below this temperature the values obtained show great uncertainty, this being due to the readiness with which the unstable modification changes to the stable form. Before equilibrium between saturated solution and unstable hydrate could be attained, the change in the solid phase consistently occurred and the solution underwent the corresponding change in concentration. The stable solubility curve of Bassett and Taylor has been re-checked, and in one or two cases minor changes in the values of the solubilities have been made.

The solution in equilibrium with the anhydrous salt at 25°, was prepared by evaporating a solution of the salt until salt just began to separate at the boiling point (151°). The mixture thus obtained was cooled to 25°, stirred for several days and the solid phase finally allowed to settle. The clear, viscous liquid thus obtained was then analyzed.

In all cases the analysis was made by weighing as oxide after precipitation as oxalate.

Precautions were taken to ensure purity of material similar to those previously employed. The solution of a high-grade calcium nitrate was treated with a considerable excess of pure and freshly ignited calcium oxide. The mixture was shaken frequently for several days and then filtered. In this way magnesium salts were removed as hydroxide. The solution was then neutralized with nitric acid and evaporated to the crystallization point.

The data obtained from the analyses of the various solutions at the various temperatures are compiled in Table I.

The point on the reflex portion of the unstable solubility curve entailed

considerable trouble in attainment. After repeated trials a solution was obtained, of the composition analyzed, in equilibrium with the unstable hydrate. That the solid phase was the unstable form was shown by bringing to the equilibrium mixture a crystal of the stable hydrate. This resulted in a rapid change of the equilibrium with separation of a considerable bulk of solid phase. It will be noted how considerable the change in concentration on the retroflex portion of the curve for small variation of the temperature, in other words, how flat the curve is around the maximum, corresponding to considerable dissociation into the components.

TABLE I.

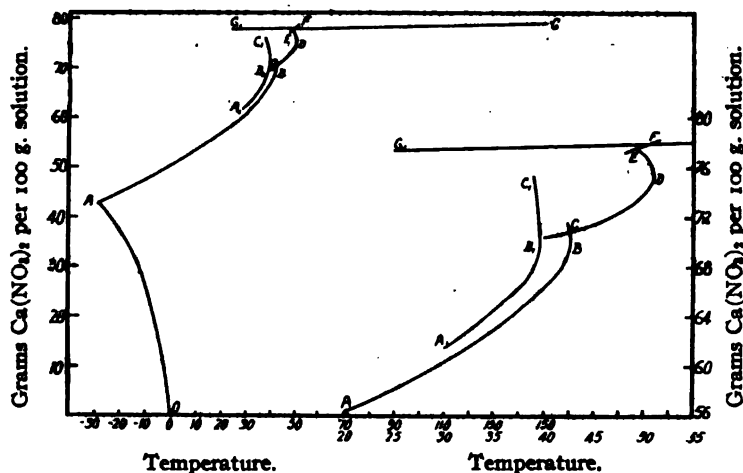
Temperature.	G. $\text{Ca}(\text{NO}_3)_2$ per 100 g. of solution.	Composition of the solid phase.	Observer.
0	50.17	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
22.2	56.88	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
25.0	57.90	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
30.0	60.16	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
30.0	61.57	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
34.0	63.66	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
35.0	62.88	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	B. & T.
38.0	64.34	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
38.0	66.65	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
39.0	67.93	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
39.6 (m. p. of hydrate)	69.50	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
39.0 (reflex pt.)	75.34	$\beta\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	T. & H.
40.0	66.21	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	B. & T.
42.7 (m. p. of hydrate)	69.50	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	B. & T.
42.4 (reflex pt.)	71.70	$\alpha\text{Ca}(\text{NO}_3)_{1.4}\text{H}_2\text{O}$	B. & T.
25.0	77.30	$\text{Ca}(\text{NO}_3)_2$	T. & H.

Discussion of the Results.

The results from the investigation are expressed graphically in Fig. 1. For the sake of completeness and to facilitate the following discussion the whole curve has been drawn employing the data of Bassett and Taylor. The new material communicated in the present paper is also plotted, for the sake of clearness, on a large scale to the right of the complete curve.

It will be seen that the two-component system calcium nitrate-water forms a very interesting example of phase equilibria, in that by use of it alone all the various possible types to be met with in phase relationships of salt hydrates may be illustrated. Curve OA represents the ice curve and point A the cryohydric point. Curves ABC and CDE, representing the solubility curves of the α -tetrahydrate and trihydrate, exemplify the case of hydrates with a true melting point such as are found with the ferric chloride hydrates. Curve $A_1B_1C_1$, that of the β -tetrahydrate, illustrates the solubility curve of a metastable hydrate with a metastable melting point, similar to that obtained with calcium chloride hexahydrate. The dihydrate, represented by Curve EF, illustrates, like sodium sulfate hecahydrate, the class of hydrates which show no true melting points but

transition points where partial fusion occurs with the formation of anhydrous salt and saturated solution. The whole diagram, therefore, shows a succession of stable hydrates, a metastable hydrate, true melting points, a metastable melting point, stable and metastable retroflex solubility curves.



An interesting point may here be emphasized with regard to the solubility curves of unstable hydrates possessing a melting point and retroflex solubility curves. As is well known, the solid phase most stable at the temperature of the experiment has, at that temperature, the least solubility. This is true even on the retroflex portions of the curves, although, as can be seen from the diagram, the concentration in grams of anhydrous salt per 100 g. of solution is greater in the case of the stable hydrate. Since, however, the calcium nitrate content of the solid hydrate is less than that of the saturated solutions on the retroflex portions of the curve, it follows that the unstable hydrate, having in accordance with the theory the greater solubility, will give rise to saturated solutions less rich in the anhydrous salt than those given by the stable form at the same temperature.

Attention may here be directed to the method described by Foote,¹ for the determination of the hydrates formed by a salt. The method described for sulfuric acid is capable of extension to salts of other acids using the corresponding acid as dehydrating agent. For example, in this connection it was shown by Bassett and Taylor that while in aqueous solutions the calcium nitrate dihydrate was difficult to prepare and stable over a short range of temperature only, still at 25°, it was readily obtained and existed in stable equilibrium over a considerable range of nitric acid

¹ THIS JOURNAL, 37, 288 (1915).

concentrations. Similarly, the three-component system $\text{BaCl}_2\text{--HCl--H}_2\text{O}$ studied by Schreinemakers at 30° ,¹ illustrates the use of hydrochloric acid to the same purpose. Indeed the method can, generally speaking, be recommended before the study of the two-component system whenever there is considerable tendency to formation of concentrated, viscous, aqueous solutions, provided of course that acid salts are not readily formed.

Finally it may be observed that the solubility of the anhydrous salt at 25° corresponds to those obtained by Bassett and Taylor at the higher temperatures and not with that obtained by D'Ans as previously mentioned.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY.]
**RADIOMETRIC MEASUREMENTS OF THE IONIZATION CON-
 STANTS OF INDICATORS.²**

[SECOND COMMUNICATION.]

BY M. G. PAULUS, J. F. HUTCHINSON AND HARRY C. JONES.

Received May 1, 1915.

An investigation of the ionization constants of methyl orange and phenolphthalein has already been published in *THIS JOURNAL* by Shaeffer, Paulus and Jones.³ In this paper a new method, based upon the absorption of light by solutions of indicators, was developed for the determination of the constants of indicators. It was shown that this method serves as well for a two-colored as for a one-colored indicator. The work recorded herein is to be regarded as a continuation of the original investigation, and the purpose is to test the applicability of the method to the determination of the ionization constant of rosolic acid. A description of the apparatus used has already been given in detail in the original paper.

Theoretical Discussion.—Considering, first of all, that rosolic acid is monobasic,⁴ the ionization constant K_i , is expressed by the simple equilibrium equation

$$\frac{(\text{H}^+)(\text{In}^-)}{(\text{HIn})} = K_i. \quad (1)$$

If, then, the hydrogen ion concentration of the indicator solution is fixed, the ratio $(\text{In}^-)/(\text{HIn})$ at equilibrium can be determined. It has been shown in the original paper⁵ that the percentage transmission of a solution, such as that of rosolic acid, containing two absorbing components is given by the equation

¹ *Z. physik. Chem.*, **68**, 89 (1909).

² This investigation has been carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones.

³ *THIS JOURNAL*, **37**, 776 (1915).

⁴ The behavior of rosolic acid as a dibasic acid will be discussed later.

⁵ *Loc. cit.*

$$\ln (I/I_0) = -Kc - K'c_1 \quad (2)$$

where c and c_1 are the concentrations of the two absorbing components; and K and K' are constants depending upon the nature of the absorbing components and the wave-length of light employed. Applying this equation to rosolic acid, let c represent the concentration of the red component, or (In) in Equation 1, and let c_1 represent the concentration of the yellow component or (HIn) . Equation 2, then, will represent the percentage transmission for some given depth of an incompletely transformed solution of rosolic acid. In a solution containing a large excess of acid $c = 0$, and Equation 2 becomes

$$\ln (I/I_0)' = -K'c_1 = -K'T \quad (3)$$

If a large excess¹ of alkali is added to the indicator solution $c_1 = 0$, and Equation 2, reduces to

$$\ln (I/I_0)'' = -Kc = -KT \quad (4)$$

where T equals the total concentration of the indicator in solution. If the percentage transmissions are determined for the same depth of solution and for the same wave-length of light, and if the total concentration of the indicator is the same in all solutions, then the values of the constants K and K' given by Equations 3 and 4, can be substituted in Equation 2, whence

$$T \times \ln (I/I_0) = \ln (I/I_0)'' \times c + \ln (I/I_0)' \times c_1 \quad (5)$$

Since the total concentration of the indicator T is always equal to the sum of the two components, $T = c + c_1$, Equation 5 reduces to:

$$c/c_1 = \frac{\ln (I/I_0)' - \ln (I/I_0)}{\ln (I/I_0) - \ln (I/I_0)''} \quad (6)$$

The ratio $c/c_1 = (\text{In})/(\text{HIn})$ can be determined from Equation 6. (I/I_0) is the percentage transmission for some given depth of the incompletely transformed solution under investigation, for some wave-length of light; $(I/I_0)'$ the percentage transmission of the indicator solution completely transformed into the yellow component, for the same wave-length; and $(I/I_0)''$ the percentage transmission for the same depth of indicator solution completely transformed into the red component, for the same wave-length of light. The total concentration of the indicator in these three solutions must, of course, be the same, but the total concentration need not be known.

Returning now to Equation 1, the method of obtaining all the data necessary for calculating the ionization constant is known, except that for determining the concentration of the hydrogen ion. This was fixed by solutions of disodium phosphate containing varying amounts of hydro-

¹ By "a large excess" is meant sufficient alkali to convert the indicator entirely into its red component.

chloric acid. The addition of hydrochloric acid converts the hydrophosphate ion almost quantitatively into the dihydrophosphate ion. The hydrogen ion concentration is given in such a solution by

$$H^+ = \frac{1.95 \times 10^{-7} (H_2\bar{P}O_4)^1}{(H\bar{P}O_4)} \quad (7)$$

If we represent by a , the concentration of the added hydrochloric acid, and by b , the concentration of the disodium phosphate, then Equation 7 becomes

$$H^+ = \frac{1.95 \times 10^{-7} \times a\alpha_1}{(b - a)\alpha_2}, \quad (8)$$

where α_1 and α_2 represent, respectively, the dissociations of the mono- and disodium phosphates present at equilibrium.

If the quantity of disodium phosphate in the solutions investigated is always kept the same, the hydrogen ion concentration can be varied simply by the addition of different amounts of hydrochloric acid. In this case the total salt concentration is constant. This is extremely desirable, as it has been shown by Rosenstein,² that neutral salts have a great effect upon the fraction of the indicator transformed. The value of the ionization constant in the case of phenolphthalein is doubled by increasing the total salt concentration from 0.03 to 0.40 N .

Preliminary Work on Rosolic Acid.—Three stock solutions were prepared, all solutions being made up at 20° with conductivity water. The stock solution of disodium phosphate was prepared from a pure sample of standard make. Its concentration was 0.1036 g. molecules per liter, the concentration being determined gravimetrically as magnesium pyrophosphate. The concentration of the stock solution of hydrochloric acid was 0.08085 N . The stock indicator solution was prepared by dissolving about 0.4 g. of an excellent sample of rosolic acid in two liters of conductivity water. The total quantity of the indicator did not dissolve, but as has been previously explained, it is not necessary to know the concentration of the indicator employed.

The incompletely transformed solutions to be tested were prepared from the stock solutions, so that all contained the same amounts of indicator and disodium phosphate, but different amounts of hydrochloric acid. This procedure was followed to keep the total salt concentration the same in all solutions. The volume of each solution was 100 cc. The percentage transmissions (I/I_0) were taken with a 20 mm. depth of each solution, and for the same five wave-lengths of light. As explained in the original article,³ the percentage transmissions were determined by a

¹ The value of the constant was taken from the work of Abbott and Bray, *THIS JOURNAL*, 31, 760 (1909).

² *THIS JOURNAL*, 34, 1128 (1912); see also *Ibid.*, 37, 804 (1915).

³ *Loc. cit.*

differential method, which avoided the necessity of introducing certain correction factors due to the glass ends with which the cells were provided.

A consideration of Equation 6 will show that the method of calculating the ratio of the red to the yellow component of any incompletely transformed indicator solution, not only depends upon the transmission of the solution under investigation, but also upon the transmission of an indicator solution containing a large excess of acid in which the indicator is totally transformed into its yellow constituent; and also upon the transmission of an indicator solution containing a large excess of alkali in which the indicator is totally transformed into its red component. Table I gives the results of a series of measurements made upon the indicator solution containing an excess of alkali. All solutions contain 50 cc. of the stock solution of rosolic acid, plus the amount of *N* NaOH indicated in the table, the solutions being in all cases diluted to 100 cc. The percentage transmissions are given for five wave-lengths of light between $\lambda = 0.56\mu$ and $\lambda = 0.58\mu$, which is the region of the spectrum employed throughout this investigation. In certain cases, the results of duplicate measurements are given, which indicate in a general way the accuracy of the results.

TABLE I.
(I/I_0) — depth of solution equals 20 mm.

1.	2.	3.	4.	5.	6. 0.5 cc. <i>N</i> NaOH.	7.	8.	9.	10.
$\lambda =$ Å U.	After 5 min.	After 10 min.	After 20 min.	After 30 min.	After 55 min.	After 5 hrs.	After 24 hrs.	After 24 hrs.	3.0 cc. after 24 hrs.
5598	22.6	16.1	12.5	10.7	9.08	7.55	6.25 6.37	6.53 6.53	9.16
5648	36.1	30.6	27.4	22.6	20.0	20.0	17.0 16.7	17.6 16.7	19.1
5698	52.3	44.8	44.2	38.8	37.9	37.0	34.5 34.5	32.2 32.2	35.6
5748	64.8	60.6	58.3	55.6	52.8	51.4	52.4 50.7	49.3 48.7	50.7
5798	77.0	73.3	71.1	68.4	64.1	64.8	66.6 66.2	63.5 63.7	66.3

Column 2, Table I, gives the percentage transmissions of an indicator solution containing 0.5 cc. *N* NaOH, the transmissions being determined within a short time after the solution was prepared. Columns 3 to 7, inclusive, give the percentage transmissions after the same solution had stood for various intervals of time up to 55 minutes. Columns 8 and 9 give the percentage transmissions of new indicator solutions containing the same amount of indicator and alkali, after these solutions had stood, respectively, for 5 to 24 hours. It will be observed that the percentage transmissions for any given wave-length of light become constant after the solutions have stood between 1 and 5 hours.

The fact that solutions of rosolic acid containing an excess of alkali become less and less transparent to yellow light on standing, clearly indicates that the concentration of the red component (I_n) present is becoming greater and greater, with a resulting decrease in the concentration of the yellow component (HI_n), since the greater the concentration of the red component the more opaque the solution becomes to yellow light.

According to the most recent views¹ concerning the cause of color production of indicators of the aurine type, the color is not due simply to the presence of a quinoid group as such, but to an inter- or intramolecular combination of the metallic phenolate with the quinoid complex. It is very probably true, in the case of rosolic acid, that this combination between the metallic phenolate and the quinoid complex takes place rather slowly, with a corresponding intensification of the red color.

It will be observed that the transmission values recorded in Column 10, Table I, of an indicator solution containing 3 cc. *N* NaOH are considerably higher than those recorded in Columns 8 and 9, for a solution containing 0.5 cc. *N* NaOH. In both cases the solutions have come to equilibrium, since it has been shown that equilibrium is established after the solutions have stood between 1 and 5 hours. When very much larger amounts of alkali are added (say 10 cc.), a very perceptible bleaching takes place. In solutions, then, containing an excess of sodium hydroxide two opposing reactions take place: first, a gradual intensification of the red color brought about very probably by a time reaction between the metallic phenolate and the quinoid complex; and second, a bleaching of the red color which is greater the larger the amount of the alkali added. Since it is necessary to know the true percentage transmission $(I/I_0)^{\%}$ of a solution completely transformed into the red component, in order to determine the ratio c/c_1 (see page 1695), it follows that the bleaching must be avoided. This result can be obtained by keeping the concentration of the alkali as small as possible, only adding sufficient to transform completely the indicator. The obvious method was to increase gradually the hydroxyl ion concentration, until the solutions were shown to be completely transformed. Table II gives the results of such a determination. All solutions contain 50 cc. of the stock solution of indicator, plus the amount of disodium phosphate and hydrochloric acid indicated in the table. All solutions were allowed to stand a sufficient length of time for equilibrium to be established.

TABLE II.
(I/I_0)[%] — depth of solution equals 20 mm.

$\lambda = \text{\AA. U.}$	1. 25 cc. Na_2HPO_4 , 1 cc. HCl. After 24 hrs.		2. 25 cc. Na_2HPO_4 , 0.5 cc. HCl. After 48 hrs.		3. 25 cc. Na_2HPO_4 , 0 cc. HCl. After 48 hrs.		4. 25 cc. Na_2HPO_4 , 0 cc. HCl. After 96 hrs.	
5598	4.44	4.35	4.68		4.68	4.76	5.00	
5648	13.7	14.0	11.1		10.8	11.0	9.6	
5698	22.8	22.8	19.4		19.4	18.8	19.0	
5748	40.0	40.0	33.3		34.1	34.9	34.5	
5798	51.6	51.0	48.4		48.4	49.4	48.8	

Solution 1, Table II, in which the hydrogen ion concentration is 0.8266×10^{-8} , gives higher values for the percentage transmissions than solu-

¹ *Am. Chem. J.*, 30, 537, 650, and 651 (1908).

tions 2 and 3, in which the hydrogen ion concentrations are, respectively, 0.4157×10^{-8} and 0.043×10^{-8} . This shows that Solution 1 is not completely transformed, since an increase in the red component and a corresponding decrease in the yellow component make the solution more opaque to yellow light. Solution 2 must, however, be completely transformed since, when the hydrogen ion concentration is still further decreased as is the case in Solution 3, the transmission values remain the same. The values of the percentage transmissions recorded in Columns 2, 3 and 4 are the values to be substituted for $(I/I_0)^n$ in Equation 6.

In order to ascertain if this same decrease in the transmissions, corresponding to an increase in the red component, would take place on standing with solutions of indicators which are incompletely transformed, four solutions were prepared containing in 100 cc.—50 cc. rosolic acid, 25 cc. Na_2HPO_4 and 1 cc., 5 cc., 10 cc. and 15 cc. of HCl, respectively.

In Table III, are given the percentage transmissions for a depth equal to 20 mm. of the above series of solutions. The transmissions were determined after the solutions had stood for intervals of 5, 16 and 24 hours. The transmission values recorded in Columns 1 and 3 were determined with the same series of solutions. A new series of solutions were prepared for the 16-hour determination, the results of which are recorded in Column 2. Solution 1 was not made up for this determination. Duplicate measurements are given in every case.

TABLE III.
(I/I_0) — depth of solution equals 20 mm.

Solution.	$\lambda = \text{\AA. U.}$	1.	2.	3.	
		After 5 hrs.	After 16 hrs.	After 24 hrs.	
No. 1 containing 1 cc. HCl Plus 25 cc. Na_2HPO_4	5598	16.7 16.3	4.44	4.35
	5648	32.7 30.2	13.7	14.0
	5698	42.8 43.2	22.8	22.8
	5748	59.1 57.4	40.0	40.0
	5798	69.7 70.3	51.6	51.6
No. 2 containing 5 cc. HCl Plus 25 cc. Na_2HPO_4	5598	30.8 30.8	25.7 25.0	26.4	26.4
	5648	39.3 39.6	35.4 35.9	37.5	35.7
	5698	52.6 51.7	48.3 40.0	50.0	49.3
	5748	66.1 64.5	60.8 60.7	60.3	59.4
	5798	72.7 74.3	71.0 71.0	70.7	70.6
No. 3 containing 10 cc. HCl Plus 25 cc. Na_2HPO_4	5598	49.0 49.0	50.7 50.7	49.0	49.1
	5648	57.8 57.8	60.0 59.3	60.0	58.8
	5698	66.7 68.3	68.7 68.7	70.6	70.6
	5748	73.8 73.4	78.5 77.7	76.2	77.4
	5798	83.3 83.6	84.2 84.2	84.4	83.0
No. 4 containing 15 cc. HCl Plus 25 cc. Na_2HPO_4	5598	66.1 67.3	68.0 67.2	67.3	67.8
	5648	72.4 74.1	74.9 74.3	76.4	76.4
	5698	81.6 80.3	81.3 80.4	81.0	79.5
	5748	83.2 83.2	87.2 87.2	85.5	85.5
	5798	88.2 89.4	90.2 90.2	87.7	87.8

An examination of the transmission values recorded for Solutions 1 and 2, Table III, show that a decrease in the transmissions of incompletely transformed solutions of rosolic acid also takes place on standing. Solution 2, in which the hydrogen ion concentration¹ is 4.484×10^{-8} , has come to equilibrium between 5 and 16 hours, as is shown by the fact that the transmission values become constant after 16 hours. In Solutions 3 and 4, in which the hydrogen ion concentrations are, respectively, 10.53×10^{-8} and 19.52×10^{-8} , equilibrium was established before standing 5 hours. This points to the conclusion that in the incompletely transformed solutions of the indicator, the more alkaline the solution the greater the time before equilibrium is established.

Results with Rosolic Acid.—For the first determination of the indicator constant K_i , solutions were used containing in 100 cc., 50 cc. rosolic acid, 25 cc. Na_2HPO_4 and 5, 10 and 15 cc. HCl , respectively.

These solutions were prepared from the stock solutions, and solutions were allowed to stand for 24 hours, which time, according to the results of the preliminary work, was amply sufficient for equilibrium to be established. In Table IV are given the percentage transmissions for a depth equal to 20 mm. of each of these solutions, the values being in every case the average of two measurements. These are the values to be substituted for (I/I_0) in Equation 6. As has previously been explained, the ratio c/c_1 also depends upon the percentage transmission $(I/I_0)'$ of an indicator solution completely transformed into the red component, and also upon the percentage transmission $(I/I_0)''$ of an indicator solution completely transformed into the yellow constituent. The transmissions $(I/I_0)'$ used are the averages of those recorded in Columns 2, 3 and 4, Table II. It was found that solutions containing 50 cc. of the stock solution of the indicator, plus the necessary amount of hydrochloric acid to convert the indicator entirely into the yellow component, were completely transparent to the five wave-lengths of light used. The transmissions $(I/I_0)''$ are therefore in every case 100%.

In Table IV the ratios $c/c_1 = (\text{In})/(\text{HIn})$ were calculated from Equation 6, and the constants K_i from Equation 1. The hydrogen ion concentrations were calculated by means of Equation 7, α_1 , and α_2 being interpolated from the percentage ionizations of monosodium and disodium phosphates at various dilutions given by Abbot and Bray.²

Another series of solutions, similar to the preceding with the amounts of acid indicated in Table V, were prepared, and allowed to stand 16 hours, in which time all of them had come to equilibrium. The percentage transmissions,³ calculated ratios, c/c_1 , and the constants K_i , are given in

¹ See page 1696.

² THIS JOURNAL, 31, 729 (1909).

³ The average values of two determinations are given.

Table V. The same values for $(I/I_0)'$ and $(I/I_0)''$ were used as for the preceding determination.

TABLE IV.

Solutions.	$\lambda = \text{\AA. U.}$	$H^+ \times 10^3$	Average percentage transmissions.	c/a .	$K_1 \times 10^4$.
1 (5 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	4.484	26.4	0.803	3.60
			36.6	0.811	3.64
			49.6	0.734	3.29
			59.8	0.920	4.13
			70.6	0.937	4.20
2 (10 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	10.53	49.0	0.306	3.23
			59.4	0.302	3.19
			70.6	0.266	2.81
			76.8	0.326	3.44
			83.7	0.329	3.48
3 (15 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	19.52	67.5	0.148	2.89
			76.4	0.136	2.66
			80.2	0.154	3.05
			85.5	0.171	3.34
			87.7	(0.223)	(4.35)

TABLE V.

Solutions.	$\lambda = \text{\AA. U.}$	$H^+ \times 10^3$	Average percentage transmissions.	c/a .	$K_1 \times 10^4$.
1 (5 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	2.533	12.1	2.28	5.77
			20.8	2.33	5.89
			32.0	2.20	5.56
			48.1	2.14	5.42
			60.9	2.22	5.63
2 (5 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	4.484	25.4	0.822	3.69
			35.7	0.847	3.81
			48.3	0.785	3.53
			60.8	0.849	3.82
			71.0	0.906	4.07
3 (10 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	10.53	50.7	0.288	3.03
			59.7	0.298	3.14
			68.7	0.293	3.08
			78.1	0.298	3.14
			84.2	0.314	3.30
4 (15 cc. HCl)..... (25 cc. Na_2HPO_4)	5598 5648 5698 5748 5798	19.52	67.6	0.148	2.89
			74.6	0.150	2.93
			80.8	0.146	2.89
			87.2	0.146	2.85
			(90.2)	(0.167)	(3.26)

The values of K_1 , Table V, show a steady decrease from 5.65×10^{-8} to 2.89×10^{-8} , as the solution becomes less alkaline. The average constant is 3.91×10^{-8} .¹ It is to be remembered that the constants were determined on the assumption that rosolic acid is monobasic. As is

¹ The value given by Salm, *Z. physik. Chem.*, 57, 496 (1907), is 1.1×10^{-8} .

well known the indicator is dibasic, and the decrease in the constants with decreasing alkalinity was expected. Rosolic acid actually dissociates in two stages according to the equations, $H_2In = HIn^- + H^+$, and $HIn^- = In^{2-} + H^+$.

Behavior of Rosolic Acid as a Dibasic Acid.—With regard to the two ions HIn^- and In^{2-} , three assumptions can be made: (1) that the intermediate ion HIn^- is yellow and the secondary ion In^{2-} is red; (2) that the ion HIn^- is red and the ion In^{2-} is yellow; (3) that both the ions HIn^- and In^{2-} are red. In the first case the ratio of the red to the yellow component will be given by

$$c/c_1 = \frac{In^{2-}}{HIn^- + H_2In} \quad (9)$$

In addition, the equilibrium equations given below have to be considered.

$$\frac{(H^+)(HIn^-)}{(H_2In)} = K_1 \quad \frac{(H^+)(In^{2-})}{(HIn^-)} = K_2 \quad (10)$$

By combining these three equations we obtain

$$c/c_1 = \frac{K_1 K_2}{H^+(H^+ + K_1)} \quad (11)$$

In the second case, when the ion HIn^- is red and the ion In^{2-} is yellow, the ratio becomes.

$$c/c_1 = \frac{HIn^-}{H_2In + In^{2-}} \quad (12)$$

and from Equations 10

$$c/c_1 = \frac{H^+ K_1}{H^2 + K_1 K_2} \quad (13)$$

In the third case, *i. e.*, when both ions HIn^- and In^{2-} are red, the ratio is given by

$$c/c_1 = \frac{HIn^- + In^{2-}}{H_2In} \quad (14)$$

$$\text{whence, } c/c_1 = \frac{H^+ K_1 + K_1 K_2}{H^2 + K_1 K_2} \quad (15)$$

Equations 11, 13, and 15 were tested by substituting the experimental values of the ratios c/c_1 and the hydrogen ion concentrations given for Solutions 1 and 4, Table V, in the equations, and solving for the constants K_1 and K_2 . The constants were then used to calculate the ratios for Solutions 2 and 3. In Table VI, are given the values of the ratios c/c_1 calculated from the various equations, and also the observed experimental ratios which are the averages of those given in Table V.

¹ The development is essentially the same as given by Rosenstein for phenolphthalein. *THIS JOURNAL*, 36, 1124 (1912).

TABLE VI.

Solution.	$H^+ \times 10^6$.	Values of c/a .			
		Observed.	Calc. by 11.	Calc. by 13.	Calc. by 15.
1.....	2.533	2.23	2.23	2.23	2.23
2.....	4.484	0.842	1.12	...	0.953
3.....	10.53	0.298	0.371	...	0.308
4.....	19.52	0.148	0.148	0.148	0.148

On the first assumption, namely, that the ion $HI\bar{n}$ is yellow and the ion $I\bar{n}$ is red, the ratios calculated by Equation 11, for Solutions 2 and 3, do not at all agree with the experimentally determined values. On the assumption that the intermediate ion $HI\bar{n}$ is red and the secondary ion $I\bar{n}$ is yellow, the constant K_2 , Equation 13, was found to be a negative quantity. This, in itself, proves the absurdity of the assumption; consequently, no ratios for Solutions 2 and 3 were calculated. On the assumption, however, that both the ions $HI\bar{n}$ and $I\bar{n}$ are red, the ratios calculated by Equation 15, agree fairly closely with the experimentally determined values. The agreement is as close as might be expected considering that in work of this character so many different sources of error are possible. The results lead to the conclusion, therefore, that rosolic acid acts as a dibasic acid, and furthermore, show that both the primary and secondary ions are intensely colored.

In the case of phenolphthalein, it has been shown by Rosenstein¹ that the colored form of the indicator is only produced in appreciable quantity when the second hydrogen of the indicator acid is replaced by the base. This is in accord with the theory already referred to,¹ that the cause of the color production is due to a combination between the metallic phenolate and the quinoid complex: since it is only where the second hydrogen is replaced that the formation of the quinoid phenolate complex is possible. In the case of rosolic acid, however, the quinoid phenolate complex can be found when the first hydrogen of the indicator acid is replaced by the base. The experimental fact, then, that the intensely colored form of the indicator is produced when the first hydrogen is replaced by the base is perfectly in accord with the theories advanced.

Summary.

1. An intensification of the red color of rosolic acid solutions incompletely transformed by the addition of alkali was found to take place when such solutions were allowed to stand, the time reaction being in all probability due to a slow union of the metallic phenolate with the quinoid complex.

2. In rosolic acid solutions containing a large excess of alkali a perceptible bleaching of the red color was also indicated.

3. The ratio (c/c_i) of the red to the yellow component has been de-

¹ *Loc. cit.*

terminated for indicator solutions of various hydrogen ion concentrations using the radiometric method developed in the original article.¹

4. The values of the ionization constant of rosolic acid calculated from the ratio c/c_1 , on the assumption that the indicator acid is monobasic, were found to decrease with decreasing alkalinity. When the hydrogen ion concentration was increased from 2.533×10^{-8} to 19.52×10^{-8} , the total salt concentration being 0.0259 *N*, the value of the ionization constant K_i was found to decrease from 5.65×10^{-8} to 2.89×10^{-8} .

5. It was found that this variation in the constants could be explained by regarding the indicator as a dibasic acid, and it was shown, furthermore, that the intensely colored form of the indicator is formed when the first hydrogen of the indicator acid is replaced by the base.

BALTIMORE, MD.
April, 1915.

THE SOLUBILITY OF MAGNESIUM CARBONATE IN NATURAL WATERS.²

BY ROGER C. WELLS.

Received May 10, 1915.

Treadwell and Reuter,³ who determined the solubility of magnesium carbonate in water under given partial pressures of carbon dioxide, found for a partial pressure of "0 mm." of carbon dioxide at 15°, 0.6410 g. magnesium carbonate and 1.9540 g. magnesium bicarbonate per liter. This is equivalent to 0.51 g. magnesium and 2.09 g. carbon dioxide per liter. Cameron and Briggs,⁴ however, found only 0.18 g. magnesium and 0.543 g. carbon dioxide per liter at room temperature after passing a current of air through the solution for a very long period. Feeling that more attention should be paid to the nature of the solid phase, I have carried out experiments that show a difference in the behavior of magnesite, the simplest natural variety of magnesium carbonate, and nesquehonite, the trihydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and, furthermore, find solutions in equilibrium with the latter substance under atmospheric conditions at 20° to contain 0.36 g. magnesium and 1.01 g. carbon dioxide per liter.

As the object of the experiments was to imitate natural conditions, the solutions were exposed to the action of outdoor air over long intervals, in order that they might come into equilibrium with the small amount of carbon dioxide in the atmosphere. The air was filtered through cotton, washed by distilled water and bubbled through the solutions contained in Jena flasks immersed in a thermostat. The thermostat was

¹ *Loc. cit.*

² Published by permission of the Director of the United States Geological Survey.

³ *Z. anorg. Chem.*, 17, 202 (1898).

⁴ *J. Physic. Chem.*, 5, 553 (1901).

not in action over night, but since no large variations of temperature were permitted and since no air was passed then it is believed that no error was introduced from this source.

Magnesite.

This mineral is usually associated with serpentine or rocks containing members of the olivine group. As a rule it is compact and amorphous, possibly a colloid, but a crystalline variety is known whose origin is probably somewhat different from that of the amorphous variety. A specimen of the amorphous variety from Placer County, Colorado, kindly supplied by H. S. Gale, of the United States Geological Survey, and used for the solubility determinations, was found on analysis to have the following composition: SiO_2 0.09, Fe_2O_3 0.11, Al_2O_3 0.09, CaO 0.05, MgO 46.82, CO_2 51.75, H_2O 0.67; sum 99.58%.

Tables I and II show the extent to which this magnesite dissolved in water alone, and in water containing as much sodium chloride as sea water, under atmospheric conditions, during periods that were practicable for laboratory observation.

TABLE I.—SOLUBILITY OF MAGNESITE IN WATER UNDER ATMOSPHERIC CONDITIONS.
(GRAMS PER LITER.)

Interval.	Mg.	Free CO_2 .	CO_2 as bicarbonate.
One hour at 20°	0.004	0.002	0.018 ¹
3 days	0.012	Trace	0.053
25 days	0.013	Trace	0.045
37 days	0.017	Trace	0.055
61 days	0.018	Trace	0.065

TABLE II.—SOLUBILITY OF MAGNESITE UNDER ATMOSPHERIC CONDITIONS IN WATER CONTAINING 27.2 G. NaCl PER LITER. (GRAMS PER LITER.)

Interval.	Mg.	Free CO_2 .	CO_2 as bicarbonate.
11 days	0.025	Trace	0.064
35 days	0.028	Trace	0.086

The Trihydrate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

If the excess carbon dioxide is expelled by a current of air at ordinary temperature from a solution containing magnesium bicarbonate and carbon dioxide the precipitate consists of well developed crystals of the trihydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, probably identical with the natural mineral nesquehonite.²

Table III shows the rate at which the changes in the solution went on. The state of the carbon dioxide was determined by titration with 0.02 *N* NaHSO_4 , first with phenolphthalein and then with methyl orange. The total carbon dioxide thus found agreed with that directly determined by

¹ The distilled water used contained several milligrams of CO_2 per liter to begin with.

² Leitmeier, *Z. Kryst.*, 47, 118 (1910). Below 6° the pentahydrate, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, was obtained.

absorption in soda-lime tubes after expulsion with HCl and boiling. Direct determinations of magnesium were also found to agree with the amounts calculated from the titrations.

TABLE III.—RATE OF EVOLUTION OF CO_2 FROM A SOLUTION CONTAINING $\text{Mg}(\text{HCO}_3)_2 + \text{CO}_2$ AT 20° WITH A GOOD STREAM OF AIR (ABOUT 5 BUBBLES A SECOND).

Time elapsed.	Mg.	Free CO_2 . G. per liter.	CO_2 as bicarbonate. G. per liter.	CO_2 as carbonate. G. per liter.	Total CO_2 .
Start	0.87	0.37	3.14	3.51
1 hour	0.87	0.17	3.10	3.27
2 hrs.	0.87	0.10	3.14	3.24
3 hrs.	0.87	0.00	3.10	0.02	3.12
5 hrs.	0.87	2.96	0.10	3.06
7 hrs.	0.87	2.67	0.22	2.89
2 days	0.87	2.39	0.37	2.76
3 days	0.87	1.83	0.64	2.47
Crystals of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ appear.					
4 days	0.83	1.69	0.66	2.35
14 days	0.61	1.45	0.38	1.83
16 days	0.53	1.03	0.44	1.47
26 days	0.43	0.88	0.35	1.23
47 days	0.39	0.84	0.29	1.13
65 days	0.38	0.83	0.28	1.11

The solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ in water under atmospheric conditions was also determined by approaching the point of equilibrium from the side of unsaturation, with the results noted in Table IV. The salt for this purpose was prepared by mixing solutions of magnesium chloride and sodium bicarbonate and washing the precipitate with water. It was proved by analysis to be the trihydrate. Air was bubbled through the solution daily for 4 days followed by a lapse of 10 days when no air was passed; the passage was then resumed daily as noted. The means of the final values of Tables III and IV are: 0.36 g. magnesium and 1.01 g. carbon dioxide per liter.

TABLE IV.—SOLUBILITY OF $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ IN WATER UNDER ATMOSPHERIC CONDITIONS AT 20° . (GRAMS PER LITER.)

Interval.	Mg.	CO_2 as carbonate.	CO_2 as bicarbonate.	Total CO_2 .
2 days	0.25	0.36	0.17	0.53
4 days	0.26	0.36	0.21	0.57
13 days	0.28	0.29	0.43	0.72
17 days	0.30	0.31	0.46	0.77
19 days	0.34	0.31	0.61	0.92
22 days	0.35	0.30	0.60	0.90
29 days	0.34	0.32	0.59	0.91

The difference in the solubility of magnesite and the trihydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is evident from Tables I and IV. Some have supposed the trihydrate to be a basic bicarbonate, $\text{MgOH} \cdot \text{HCO}_3 \cdot 2\text{H}_2\text{O}$. Whether this is so or not, there is a difference in the state of the carbon dioxide in the two solu-

tions; the proportion existing as carbonate increases with the magnesium concentration, although in the more concentrated solutions (Tables III and IV) the bicarbonate ion concentration still exceeds that of the carbonate.

If the trihydrate is regarded as a carbonate its solubility-product may be calculated from the data of Tables III and IV as follows:

$\text{Mg} = 0.36 \text{ g. per liter} = 0.015 \text{ mole.}$

$\text{CO}_2 \text{ as carbonate} = 0.30 \text{ g. per liter} = 0.0068 \text{ mole CO}_2.$

The product of the two concentrations just stated gives

$$(\text{Mg})(\text{CO}_2) = 0.0310.$$

This is apparently a maximum value of the solubility product of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at 20° since complete dissociation and no hydrolysis are assumed. There appear to be too many uncertainties in the ionic concentrations to attempt to compute a minimum value.

Natural Waters.

It is interesting to note in this connection that the highest concentration of Mg reported in a river water in the United States is 0.077 g. per liter, in the Wabash River near Logansport, Indiana, October, 1906.¹ This water was practically neutral, the HCO_3 reported being 0.276, equivalent to 0.200 g. CO_2 per liter, and NaCl about 1.3 g. per liter.

A slightly higher content of Mg than the above was found in Pyramid Lake, Nevada, in 1884,² viz., 0.080 g. Mg per liter, with 0.360 total CO_2 , and about 2.5 NaCl. The ocean, however, has 1.30 g. Mg and about 0.10 g. CO_2 per liter.

With the data now at hand, it appears that none of these natural waters is saturated with respect to the trihydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

On the other hand, either they are all supersaturated with respect to magnesite or else the solubility found for magnesite had not yet reached its maximum value.

Summary.

(1) Under atmospheric conditions it appears possible to attain practically the same state in a solution saturated with $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, whether one starts with a solution containing an excess of magnesium bicarbonate or with the pure trihydrate and water, but the adjustment occurs very slowly. The solution finally contains 0.36 g. magnesium and 1.01 g. carbon dioxide per liter at 20° .

(2) The solubility found for magnesite, however, is much smaller, viz., 0.02 g. magnesium and 0.07 g. carbon dioxide per liter.

(3) Certain natural waters, freely exposed to the atmosphere, appear to be supersaturated with respect to magnesite but none approaches very closely to the point of saturation of the trihydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.

¹ Dole, U. S. Geological Survey, *Water-Supply Paper*, 236, 108 (1909).

² Clarke, U. S. Geological Survey, *Ibid.*, 364, 30 (1914).

[CONTRIBUTION FROM THE OFFICE OF PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

ON THE FACTOR TO BE USED FOR THE CALCULATION OF THE PHOSPHORIC ACID IN NEUMANN'S METHOD.¹

By S. L. JODIDI.²

Received February 15, 1915.

The method of Neumann³ for the determination of phosphorus is now frequently used by physiological chemists. The method depends on the precipitation of the phosphorus as ammonium phosphomolybdate from an acid solution containing 10% of ammonium nitrate and the titration of the precipitate with 0.5 *N* sodium hydroxide. The precipitate is washed with cold water and is boiled with an excess of the standard alkali to expel the ammonia which it contains. Assuming that the precipitate has the composition $12\text{MoO}_3 \cdot (\text{NH}_4)_2\text{PO}_4 \cdot 2\text{HNO}_3$, after the expulsion of the ammonia each mol should require 56 mol of 0.5 *N* sodium hydroxide and 1 cc. of the alkali should be equivalent to $31.04/56 = 0.554$ mg. P, which is the factor given by Neumann. Heubner⁴ has recently shown that the factor is too low and proposes the factor 0.57. Wardlaw⁵ also claims that the factor is too low and that it varies with the amount of phosphorus present. Having occasion to use the methods in connection with a biological investigation into the chestnut bark disease, we have made a careful redetermination of the factor and have obtained results essentially in agreement with those of Heubner.

Series A.—Twenty-four grams of disodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, were dissolved in 4 l. of water. Portions of 100 cc. each were analyzed by the method of Fresenius⁶ (a) and of Schmitz⁷ (b) giving:

(a) 0.2064, 0.2058, 0.2068, 0.2074, 0.2071, 0.2068, 0.2070, 0.2068; mean 0.2068 g. $\text{Mg}_3\text{P}_2\text{O}_7$, equivalent to 0.5758 mg. P per cc.

(b) 0.2050, 0.2050, 0.2060, 0.2059, 0.2056; mean 0.2055 g. $\text{Mg}_3\text{P}_2\text{O}_7$, equivalent to 0.5723 mg. P per cc.

(c) Direct ignition of 50 cc. portions gave 0.1245, 0.1249, 0.1248, 0.1248, 0.1248 g. $\text{Na}_4\text{P}_2\text{O}_7$, equivalent to 29.09 mg. P. One cubic centimeter of the solution may, therefore, be assumed to contain 0.5766 mg. P.

Precipitation.—Ten, 20 or 40 cc. of the above solution were placed in a flask with 10 cc. of a mixture of equal volumes of concentrated sulfuric

¹ Published by permission of the Secretary of Agriculture.

² The writer wishes to acknowledge his indebtedness to Mr. E. H. Kellogg for assistance in carrying out the analyses reported in this paper.

³ *Z. physiol. Chem.*, **37**, 129 (1902-3).

⁴ *Biochem. Z.*, **64**, 393 (1914).

⁵ *C. A.*, **8**, 3540 (1914).

⁶ "Quant. Anal.," 6th Ed., I, 402 (1903).

⁷ *Z. anal. Chem.*, **43**, 279 (1904); **44**, 333 (1905); **45**, 512 (1906).

and nitric acids, 75 cc. of a 50% ammonium nitrate solution and enough water to make, with the 10% solution of ammonium molybdate (usually 40 cc.), a total volume of 250 cc. The solution was warmed to 80° before the addition of the molybdate solution. The stoppered flask was then vigorously shaken for a minute or two and after settling for 15 minutes the liquid was decanted through a 12½ cm. folded filter. The precipitate was shaken with 150 cc. of ice water, then the liquid was decanted and this was repeated three or four times. The washed filter was placed in the flask containing the precipitate and reduced to pulp with 150 cc. of distilled water. An excess of 0.5 *N* NaOH was added, the solution boiled for 15 or 20 minutes to expel the ammonia and, after cooling, the excess of alkali was titrated back with 0.5 *N* H₂SO₄.

The following results were found: Using 40 cc. of the phosphate solution, the factors were 0.577, 0.572, 0.577, 0.571, 0.568. Using 20 cc., 0.578, 0.574, 0.574, 0.577, 0.576. Using 10 cc., 0.576, 0.579, 0.568, 0.582, 0.582. Mean, 0.575.

Series B. Primary Potassium Phosphate as Standard Substance.—A solution was employed which contained in each cc. 0.378 mg. of P, as found by determinations according to the Fresenius and the Schmitz gravimetric methods. Twelve portions of this solution of 25 cc. each were titrated according to the Neumann method and the following volumes of 0.5 *N* sodium hydroxide were required, corrected for the volume required in the titration of a blank solution containing no phosphate, but traces of carbonic acid and material resulting from the disintegration of the filter paper. The amount of this correction, which is applied in all cases, is 0.2 cc. of the alkali solution, leaving as the corrected volumes:

16.82, 16.95, 16.70, 16.95, 16.61, 16.80, 16.51, 16.48, 16.97, 16.45, 16.80 and 16.80 cc. of 0.5 *N* NaOH.

The mean factor calculated from these titration volumes is 0.568.

Series C. Secondary Ammonium Phosphate as Standard Substance.—An aqueous solution was used which contained in each cc. 0.31618 mg. P, as found by determination according to the method of Fresenius (a), or 0.31607 mg. P according to the method of Schmitz (b). Twelve 50-cc. portions of this solution were titrated according to the Neumann method. The volumes of standard sodium hydroxide required, corrected for the volume found in the titration of a blank analysis, were as follows:

27.80, 27.65, 27.65, 27.64, 27.60, 27.60, 27.60, 27.60, 27.42, 27.61, 27.53, 27.60 of 0.5 *N* NaOH.

The mean factor calculated from these figures is 0.573 (a), and 0.573 (b).

Series D. Phosphoric Acid as Standard Substance.—For this series a dilute solution was used which contained in each cc. 0.35254 mg. P as

found by the gravimetric analysis according to the Fresenius method (a), or 0.35110 mg. P according to the Schmitz method. Eighteen portions of this solution of 50 cc. each were titrated according to Neumann's method. The volumes of 0.5 *N* sodium hydroxide required, corrected for the blank analysis, were as follows:

31.00, 31.15, 30.85, 31.12, 31.13, 30.95, 31.15, 31.00, 31.13, 30.98, 31.20, 30.95, 31.05, 30.95, 31.02, 31.00, 31.08, 31.15.

The average factor calculated from these data is 0.568 (a) or 0.566 (b).

Series E. Primary Potassium Phosphate as Standard Substance.—

The solution used for this series contained in each cc. 1.51540 mg. P as found by the gravimetric analysis according to the method of Fresenius (a), or 1.50767 mg. P as found by the method of Schmitz (b). Twenty-four portions of this solution of 10 cc. each were titrated according to the Neumann method. The (corrected) volumes of 0.5 *N* sodium hydroxide required were as follows:

26.58, 26.54, 26.60, 26.51, 26.54, 26.50, 26.50, 26.42, 26.50, 26.51, 26.60, 26.55, 26.60, 26.52, 26.60, 26.60, 26.40, 26.42, 26.48, 26.45, 26.58, 26.50, 26.51, 26.45. •

The mean factor calculated from these data is 0.572 (a), or 0.569 (b).

The average factor for all five series is 0.571, based on the Fresenius gravimetric method (a), or 0.570, based on the Schmitz gravimetric method (b).

Conclusions.

(1) While Neumann's method, as modified by Gregersen, is both accurate and reliable, the factor (0.554) used for calculating the phosphoric acid is too low.

(2) The results presented in this paper fully corroborate the factor 0.57 as being very nearly correct, under the conditions outlined in this paper.

(3) Gregersen's modification to overtitrate the dissolved yellow precipitate with 0.5 *N* H₂SO₄, with a view to remove the carbon dioxide present by boiling, and then titrate back with 0.5 *N* NaOH, while in principle correct, is inconvenient since it increases the time required for each individual analysis.

(4) Instead of Gregersen's modification, it is best to run a blank analysis—or better several blank analyses—which compensates the errors due (a) to impurities (phosphorus) present in the reagents employed, (b) to carbon dioxide contained in the liquids to be titrated, and (c) to the acidity caused by the action of the boiling standard alkali on the filter paper. The figure secured for the blank analysis is to be subtracted from the acidimetric analysis proper. With uniform work the same blank may be applied to one or even several series of phosphoric acid estimations.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CONNECTICUT AGRICULTURAL COLLEGE.]

THE ESTIMATION OF URANIUM AND PHOSPHORUS.

By H. D. NEWTON AND J. L. HUGGER.

Received March 8, 1915.

It has been shown by Newton¹ that ferric iron in sulfate solution can be quickly and accurately estimated by reducing with titanous sulfate, oxidizing the excess of titanous salt with bismuth trioxide, filtering off the excess of bismuth trioxide and reduced bismuth, and titrating the resulting clear solution with a 0.1 *N* solution of potassium permanganate. As it was afterwards discovered that uranyl salts in sulfate solution were apparently reduced by titanous sulfate to the uranous condition, the present investigation was undertaken for the purpose of applying the above method to the estimation of uranium and to the estimation of phosphorus after the latter had been precipitated as ammonium-uranyl phosphate.

For this work a solution of titanous sulfate of convenient strength was prepared as follows: To 100 cc. of sulfuric acid were added little by little and with continual stirring 25 g. portions of the best hydrous c. p. titanium oxide, the whole being kept constantly heated to the fuming point of the acid. The resulting pasty mass was allowed to come to room temperature and cautiously transferred to a beaker containing about 200 cc. of cold water. After standing a short time the somewhat cloudy solution of titanous sulfate was filtered, reduced to the titanous condition by means of zinc, and then filtered directly into about two liters of recently boiled distilled water contained in a reservoir to which a Squibb's automatic buret and a hydrogen generator were immediately attached. By this means the easily oxidized titanous sulfate was kept under a constant pressure of hydrogen and measured amounts of the solution were drawn as wanted. As it was convenient to know the strength of the titanous sulfate solution it was titrated directly against a 0.1 *N* solution of potassium permanganate.

An approximately 0.1 *N* solution of uranyl sulfate was obtained by treating an equivalent amount of uranyl acetate of tested purity with sulfuric acid, filtering and diluting to the required volume. This solution was standardized in the gravimetric way by precipitating the uranium by ammonia, washing with dilute ammonium nitrate solution, igniting and weighing as U_2O_5 .

A phosphate solution was obtained by dissolving about 6.359 g. of microcosmic salt in a liter of water, the solution being afterwards standardized by use of the magnesium pyrophosphate method as outlined by B. Schmitz.²

¹ *Am. J. Sci.*, 25, 343 (1908).

² F. P. Treadwell's "Analytische Chemie," 1911.

The potassium permanganate solution of approximately 0.1 *N* value was exactly standardized by titrating against carefully weighed portions of purified sodium oxalate previously dissolved in a convenient volume of water, acidulated with 1:1 sulfuric acid and heated to 80°. This method is the one recommended by the Bureau of Standards when using sodium oxalate as a standard in volumetric analysis and is exactly described in their Circular, Number 40. The sodium oxalate here used was kindly furnished by the above-mentioned Bureau.

A bismuth trioxide must be taken which shows no appreciable reducing action toward potassium permanganate. A number of 2 g. lots of the sample used, when dissolved in sulfuric acid, cooled, and diluted, were permanently colored by the first drop of 0.1 *N* solution of potassium permanganate.

The Estimation of Uranium.

In preliminary experiments it was found that bismuth trioxide had no appreciable oxidizing action on uranous salts. Table I contains results obtained by titrating with permanganate the uranous solution left after reducing with zinc a measured amount of uranyl sulfate, cooling, adding a gram of bismuth trioxide, and filtering.

TABLE I.—DATA SHOWING LACK OF OXIDIZING EFFECT OF BISMUTH TRIOXIDE ON URANYL SULFATE.

KMnO ₄ used, cc.	UO ₃ present, g.	UO ₃ found, g.	Error, g.
8.01	0.1083	0.1088	0.0005+
7.91	0.1083	0.1074	0.0009—
7.97	0.1083	0.1082	0.0001—
7.98	0.1083	0.1084	0.0001+
7.93	0.0183	0.1077	0.0006—
8.00	0.1083	0.1086	0.0003+
7.95	0.1083	0.1080	0.0003—

In Table II are recorded results obtained when titanous sulfate was used as the reducing agent. For these experiments measured amounts of uranyl sulfate were run into an Erlenmeyer flask of 150 cc. capacity and followed by a slight excess of titanous sulfate solution. Enough concentrated sulfuric acid was then added to make the solution approximately 16% acid by volume. (It was found that uranyl salts are more easily reduced and when reduced much more stable in an acid solution of this concentration than in one that is weaker.) The flask and contents were then cooled under the tap, a small amount of bismuth trioxide was added (enough in each case to oxidize the excess of titanous sulfate) and the flask then left to stand a minute or two with occasional shaking. By the use of the filter pump and a platinum cone well padded with asbestos the solution was quickly filtered free from bismuth trioxide and reduced bismuth, the asbestos pad carefully washed three or four times with a 16% sulfuric acid solution and the combined filtrates titrated with

standard potassium permanganate. As the titanous sulfate solution contained a small amount of iron, a slight correction had to be made in the permanganate reading. This correction was easily and accurately made by a method of estimating iron in the presence of titanium as worked out by Gooch and Newton.¹

TABLE II.—DATA ON TITRATION OF URANIUM AFTER REDUCTION BY TITANOUS SULFATE IN PRESENCE OF BISMUTH TRIOXIDE.

KMnO ₄ used, cc.	UO ₂ present, g.	UO ₂ found, g.	Error, g.
4.03	0.0541	0.0545	0.0004+
4.06	0.0541	0.0549	0.0008+
8.06	0.1083	0.1092	0.0009+
8.03	0.1083	0.1088	0.0005+
7.96	0.1083	0.1079	0.0004—
12.03	0.1624	0.1631	0.0007+
12.00	0.1624	0.1626	0.0002+
12.00	0.1624	0.1626	0.0002+
12.00	0.1624	0.1626	0.0002+
16.03	0.2166	0.2173	0.0007+
16.00	0.2166	0.2169	0.0003+
16.03	0.2166	0.2173	0.0007+
16.03	0.2166	0.2173	0.0007+

As 1 cc. of 0.1 *N* permanganate corresponds to 0.01350 + g. of uranium dioxide and one drop or one-thirtieth of a cc. corresponds to 0.00045 + g. of uranium dioxide, it appears that any appreciable error in the process is probably due to the reading of the end point.

The Estimation of Phosphorus.

It has long been known that under proper conditions an alkali phosphate is completely precipitated by adding to it an excess of uranyl nitrate. In using the above reaction for the estimation of phosphorus when a separation of the ammonium-uranyl phosphate is involved, the process of filtration has always been the principle difficulty. In fact, E. F. Kern² made the statement that owing to its extreme fineness, ammonium-uranyl phosphate could not be filtered successfully through a Gooch crucible. Pulman³ in his paper on "The Estimation of Uranium and Uranyl Phosphate" which involved the filtering of the finely divided ammonium-uranyl phosphate, after giving Kern's statement, wrote of his own experience as follows:

"It was found that the precipitate went through two ashless filter papers (Schleicher and Schüll, No. 589), and also that an asbestos felt of ordinary tightness in a Gooch crucible would not entirely retain the precipitate. By shaking up the flask containing the asbestos, however, allowing it to settle a minute and then pouring off the particles still in suspension, a very finely divided asbestos was obtained, which when poured

¹ *Am. J. Sci.*, 23, 365 (1907).

² *THIS JOURNAL*, 23, 710 (1901).

³ *Am. J. Sci.*, 16, 229 (1903).

upon the felt made in the ordinary way, was found to give a pad of such tightness that the filtrate obtained from the ammonium-uranyl phosphate was perfectly clear."

And in conclusion he writes:

"The only objection to the process is that the filtering and washing of the precipitate are apt to be slow, especially when large amounts of the material are being treated."

When using the Gooch crucible our experience was similar to that of Pulman, two to three hours being sometimes needed to complete the filtering process when larger amounts of microcosmic salt were taken for analysis. It was thought that a perforated platinum cone lined with an asbestos felt would allow of faster filtering and still retain the finely divided ammonium-uranyl phosphate. A few experiments with a 2.5 in. cone sufficed to show that not only did the liquid filter much faster, but also that it was not necessary to use an extremely fine asbestos, because the ordinary asbestos as usually prepared for the Gooch crucible (when put on with some care) answered the purpose quite as well. With the help of this filtering cone, experiments were carried on in the effort to adapt the previously described method for the estimation of phosphorus.

The process as finally adapted is as follows: a measured amount of standard microcosmic salt solution was drawn into a 250 cc. beaker and a mixture of 10 g. of ammonium acetate, freshly prepared by neutralizing concentrated ammonium hydroxide with 50% acetic acid, and 5 cc. of glacial acetic acid was added. The volume was then made up to 150 cc. and the solution heated nearly to the boiling point. An excess of uranium nitrate was then slowly added with constant stirring, after which the beaker and contents were kept heated nearly to the boiling point for half an hour. After cooling to room temperature the resulting ammonium-

TABLE III.—INDIRECT DETERMINATION OF PHOSPHORUS IN AMMONIUM-URANYL PHOSPHATE.

KMnO ₄ used, cc.	UO ₃ equiv. to P ₂ O ₅ present, g.	UO ₃ found, g.	P ₂ O ₅ present, g.	P ₂ O ₅ equiv. to UO ₃ found, g.	Error on P ₂ O ₅ , g.
3.3	0.0477	0.0470	0.01183	0.0116	0.0002—
3.35	0.0477	0.0479	0.01183	0.0118	0.0000
3.35	0.0477	0.0477	0.01183	0.0118	0.0000
3.33	0.0477	0.0474	0.01183	0.0117	0.0000
3.3	0.0477	0.0470	0.01183	0.0116	0.0002—
6.7	0.0954	0.0959	0.02367	0.0237	0.0001+
6.65	0.0954	0.0952	0.02367	0.0236	0.0000
6.63	0.0954	0.0949	0.02367	0.0235	0.0001—
6.63	0.0954	0.0949	0.02367	0.0235	0.0001—
9.96	0.1431	0.1428	0.03550	0.0354	0.0000
9.95	0.1431	0.1427	0.03550	0.0353	0.0001—
9.95	0.1431	0.1427	0.03550	0.0353	0.0001—
13.26	0.1909	0.1903	0.04734	0.0472	0.0001—
13.33	0.1909	0.1913	0.04734	0.0474	0.0001+
13.3	0.1909	0.1909	0.04734	0.0473	0.0000

uranyl phosphate ($\text{UO}_2\text{NH}_4\text{PO}_4$) was filtered on an asbestos felt contained in the platinum cone which had been previously moistened with a 2% solution of ammonium acetate. After carefully washing the precipitate with the 2% ammonium acetate solution the cone and contents were transferred to a funnel of convenient size and the precipitate was dissolved and washed into a 150 cc. Erlenmeyer flask with the use of a 16% solution of sulfuric acid. This solution was then treated in turn with titanous sulfate and bismuth trioxide and titrated with potassium permanganate exactly as described in the process for the estimation of uranium. The results obtained are given in Table III.

STONRA, COGN.

EXPERIMENTS ON THE DISTILLATION OF LIQUID AIR IN A MAGNETIC FIELD.¹

By R. S. McBURR.

Received April 20, 1915.

In a letter to the Bureau of Standards dated February 8, 1912, Mr. A. Cressy Morrison of New York City, suggested that the magnetic properties of liquid oxygen were such as perhaps to make possible an improvement in the separation of oxygen and nitrogen by distillation of liquid air in a strong magnetic field and requested the Bureau to investigate this point. No extended search of the literature was made, but it was believed that this possibility had not been previously tested. Although there was no evident theoretical ground for the belief that the separation might be improved by this method, the possibilities seemed sufficient to justify the Bureau in making the preliminary tests which are described below.

It was found necessary to use small Dewar tubes so that the evolution of the gas would be sufficiently slow and uniform to make possible accurate sampling at different stages of the distillation. For each comparison the tubes, which were about 2.8 cm. inside diameter and 20 cm. long, were first filled with a sample of the liquid air to chill them, then emptied, filled with equal quantities (25 to 50 cc.) of the liquid and one was placed in position between the poles of a powerful electromagnet and the other entirely outside the magnetic field.

Samples of the gases coming off from the tubes were collected over water at known intervals and analyzed. By comparison of the results obtained from the two simultaneous distillations, the influence of the magnetic field was determinable. Since the speed of evaporation could not be made exactly the same in the two distillations which were to be compared, the quantity of gas evolved during the intervals between collection of samples was measured roughly and the comparison between dis-

¹ Published with the permission of the Director, Bureau of Standards, Washington.

tillations made on the basis of percentage of the total samples evaporated. From the analyses of the samples and the known intervals expressed in percentage of total gas, the curves were drawn to show the difference in composition of the gas given off at different stages of the distillation. From these results values were calculated to show approximately the composition of the liquid at different stages of the distillation.

In the first comparison the tube was placed directly between the poles of the magnet, giving a field of approximately 10,000 lines of force per square centimeter, but in the other three comparisons this field was directed by placing beneath the tube and in contact with one pole piece a small iron block so shaped as to increase the intensity of the field through the space occupied by the liquid. Under these conditions it was impossible to estimate with any precision the exact strength of this field through the liquid; without filings and block it would have been one of 8,000 lines of force. In the last comparison both the tubes contained, in addition to the liquid air, slightly less than 20 cc. of fine iron filings, suggested by Mr. Morrison as a means of directing the field.

In each experiment the rate of evaporation was slightly (5-10%) greater in the magnetic field, which may have had some influence on the separation. This effect may have been because of difference in the tubes themselves, difference in radiation and temperature conditions (one tube being warmed slightly by proximity to the poles of the magnet) or because of the larger liquid surface, caused by the attraction of the liquid toward the poles.

By examination of the figures it can be seen that in each comparison less oxygen came off during the early part of the distillation in the magnetic field than in a similar distillation outside the magnetic field. It is evident, therefore, that there was a tendency toward a better separation and it appears that the magnetic field has some beneficial influence upon the separation, although the limited number of experiments made did not conclusively prove this point. The results of Plate 4, when compared with those given in Plates 2 and 3, indicate that the filings, if of any influence, did not improve the separation.

The separation of two miscible liquids of approximately the same boiling point by a fractional distillation depends, of course, primarily upon the difference in the partial vapor pressure of each of the constituent liquids at the boiling point of their mixtures. Unless we assume, therefore, that the vapor tension of liquid oxygen is, in effect, changed by the influence of a strong magnetic field (due either to real change in the equilibrium pressure or to a mechanical holding back of oxygen in the field) it is difficult to explain why such field should produce any effect upon the fractional separation of the gases.

It has been impossible for the author to continue this investigation

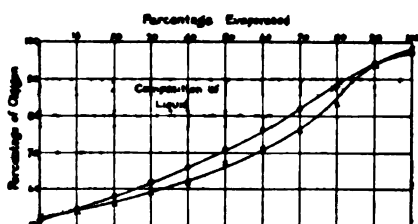
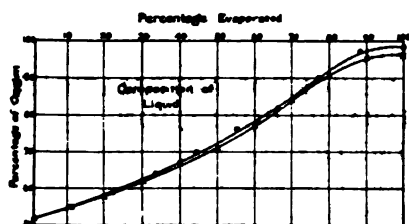
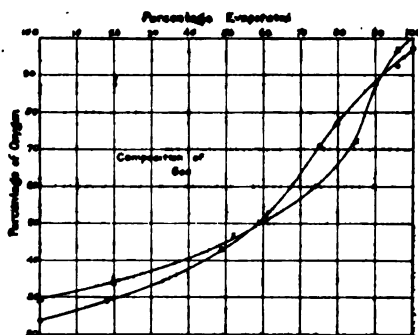
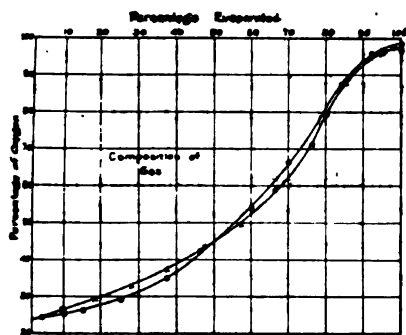


PLATE 1

PLATE 2

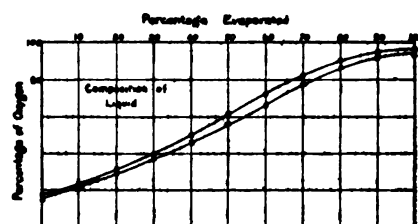
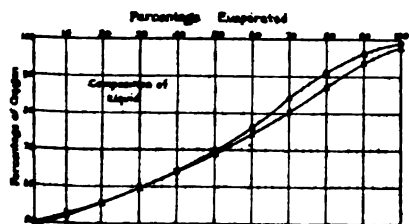
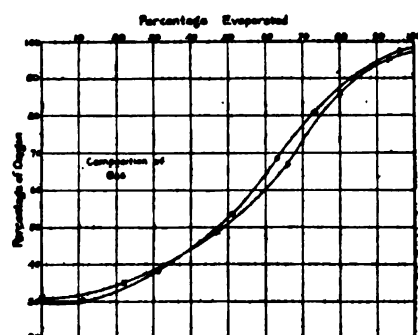
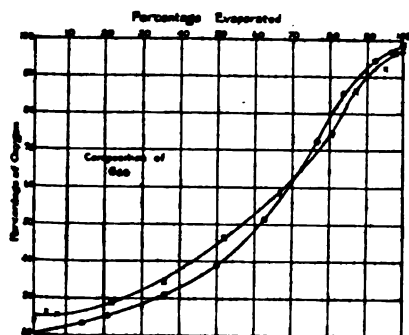


PLATE 3.

PLATE 4

CHARTS SHOWING RELATIVE CHARACTER OF DISTILLATION CURVES OF LIQUID AIR

x Ordinary distillation.

o Distillation in magnetic field.

in order to determine the influence of the many important factors which would affect the results and it, therefore, is undesirable to draw any final conclusions as to the magnitude or the importance of the separation of the gases by distillation within a magnetic field either upon a small or a large scale.

The author desires to express this thanks for the assistance rendered by Mr. F. J. Bates and Mr. F. P. Phelps in the operation of the large magnet and in the magnetic calculations and to Mr. F. S. Durston for the preparation of the liquid air required for the work.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

A SYNThERMAL REGULATOR, A DEVICE FOR AUTOMATICALLY MAINTAINING AN ADIABATIC CONDITION IN CALORIMETRY.

BY THEODORE W. RICHARDS AND GEORGE D. OSGOOD.

Received April 26, 1915.

The method of adiabatic calorimetry, as recently developed in the Harvard Chemical Laboratories, demands that the bath surrounding the calorimeter should be changed in temperature at the same rate as the calorimeter itself, so that no heat should be lost or gained during the calorimetric determination. The outside bath has therefore, been heated or cooled either by a suitable chemical reaction, or by hot or cold water, or by electricity,¹ so as to keep pace with the inside. Heretofore this quantitative identity of temperature has usually been established from moment to moment by the experimenter, who has observed both temperatures, and acted accordingly. That this technique is feasible and accurate has been abundantly proved; but, nevertheless, with quick reactions the method makes considerable demands upon the operator; accordingly, it seemed worth while to arrange an automatic device for relieving him of strain. Such a device might be called a "synthermal regulator."

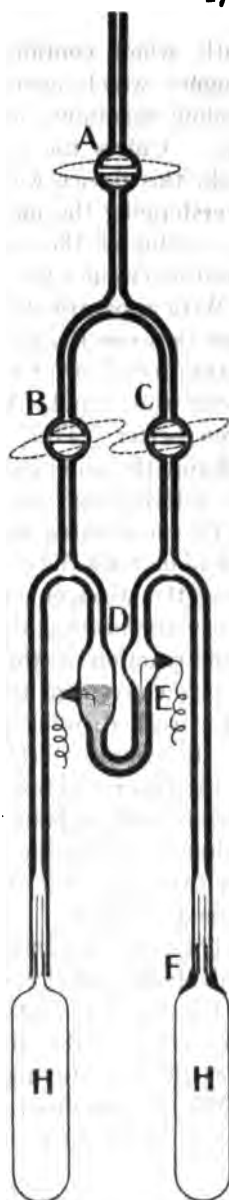
Obvious methods for accomplishing this end will occur to any one familiar with this kind of problem. A multiple thermocouple or a pair of resistance thermometers might be connected with a delicate galvanometer in such a fashion that any inequality in the temperature of the two baths would cause a deflection in a galvanometer, and thus through a relay operate a mechanism for equalizing the temperature, but it would be difficult to provide an adequate relay. A differential mercury-, or, better, a differential gas-thermometer might be used to attain the object sought, and this seemed much more promising. Because the relay seemed to be the

¹ Richards, *THIS JOURNAL*, 31, 1280 (1909); see also Benedict and Higgins, *Ibid.*, 32, 462 (1910).

crucial part of the contrivance, and because the last-named method requires a less sensitive relay than the others, it was tested first, and is described herewith. With a differential gas thermometer, in which contact is made between a very fine platinum point and a small meniscus, a fairly strong electric current may be sharply made and broken; and this, through a common long-distance telegraph relay, can govern a powerful current capable either of directly heating the outside bath or of operating any desired mechanism for this purpose.

The differential thermometer took the form illustrated in Fig. 1. Two rounded copper or silver cylinders, holding each about 28 cc., were attached by de Khotinsky cement or sealing wax (afterwards covered with paraffin to protect from caustic liquids) to a very narrow glass U tube (1.5 mm. diameter) with bulbs of familiar form. Suitable stopcocks were provided above so that the whole contrivance could be filled with hydrogen (chosen because of its great conductivity) and conveniently adjusted. A finely pointed platinum wire, containing 8% of iridium, was sealed into one of the bulbs so as to make contact with mercury at the widening of the capillary U-tube. This differential thermometer is highly sensitive, quickly making and breaking contact within $1/100^{\circ}$. It should be set up with the platinum wire outward, so as to make the current when the inner vessel is the warmer. The electromotive force of the current employed should be moderately low, to diminish sparking; and the hydrogen must be pure to avoid combustion, because the removal of hydrogen in this way may cause changes in the setting. The current thus made and broken is sent through a good relay as already indicated.

With a regulating current thus made and broken, it is possible, as stated, to operate a variety of mechanisms for regulating the temperature of the outer bath of the calorimeter. In our first experiments we used the strong current for turning on and off the flow of sulfuric acid into the outer



SYNTHETICAL REGULATOR.

(About $1/3$ actual size.)

- A, B, C—Glass stopcocks for filling and regulation.
- D—U-tube with bulbs containing mercury.
- E—Very finely pointed platinum wire sealed in to make mercury contact.
- F—Cement joint attaching HH, metal bulbs.

bath, which contained alkali; the current was led through an electromagnet which operated a plunger-valve in the delivering vessel. For cooling reactions, ice-water could obviously be delivered in a similar way. Unless the size of the jet is rather carefully proportioned to its task, this device was found at times to admit too much liquid at once, overstepping the mark; we overcame this difficulty, with a constant jet, by cutting off the current every few seconds with the help of a constantly rotating circular key.

With apparatus thus constituted, it was found that equality in temperature between the inside and outside vessels could be usually maintained within 0.02° , or at most 0.03° , even when the rise in temperature in the baths was rapid. With slow temperature changes the adjustment is even better. Thus it is capable of rendering real service in adiabatic calorimetry, and might also be useful in regulating a bath around apparatus for determining freezing points, or in other similar exigencies.

This apparatus was devised in the autumn of 1912. More recently, one of us, with the collaboration of Dr. S. Tamaru, has used it in a different way: the stronger current of electricity from the relay was employed directly for heating the outside bath. Although not so suitable for very rapid reactions as the method of adding sulfuric acid to alkali, this method is very convenient for moderately slow ones; and we found that the regulator worked sufficiently well for many purposes when used in this way. In the course of this later work the importance of equality of pressure in the two metal bulbs at the moment of electrical contact became evident. This is easily adjusted by the stopcocks and slight tilting of the apparatus. Otherwise, of course, the quantity $\Delta p/\Delta t$ may be perceptibly different on the two sides, and, therefore, a progressing deviation of the two temperatures may occur.

The chief difficulty with very rapid reactions seems to be the lack of equable distribution of the heat, especially in the inner calorimeter vessel. If the different parts of this vessel are unequal in temperature, of course the action of the differential thermometer will be irregular. Evidently very efficient stirring is necessary in both the inner and the outer vessel.

We are indebted to the Carnegie Institution of Washington for much of the apparatus used in these experiments.

Summary.

In brief, a delicate differential hydrogen thermometer with a sensitive mercury contact was devised. This, with the help of a relay, enabled a stronger current to operate a heating or cooling mechanism for causing one bath to follow the temperature of another within 0.03° . The apparatus which may be called a "synthermal regulator," is of service in adiabatic calorimetry, or in other cases where identical but changing temperatures are desired in two contiguous vessels.

[CONTRIBUTION FROM THE LABORATORY OF PLANT PHYSIOLOGY, HARVARD UNIVERSITY.]

AN IMPROVED QUARTZ MERCURY-VAPOR LAMP FOR BIOLOGICAL AND PHOTOCHEMICAL INVESTIGATIONS.

By W. T. BOVIN.

Received April 29, 1915.

In a former paper¹ the writer described a simple quartz mercury-vapor lamp for photochemical investigations. In the present paper a much more powerful lamp is described. The improved lamp is so simple, efficient and durable that the employment of ultraviolet light in biological and chemical investigations should be decidedly facilitated by its use.

The principles of the mercury air-pump have been incorporated into the design so that no pump, other than an ordinary water aspirator, is required to exhaust the lamp to a very high vacuum. This feature not only does away with all troubles connected with the original exhaustion of the lamp, but makes it possible to re-exhaust the lamp quickly and easily at any time. The lamp can be re-exhausted without in any way disturbing the chemical substances under investigation and without interrupting the exposure for more than a fraction of a minute. The length of life of the lamp is, therefore, limited only by the durability of the quartz. A maximum of efficiency is obtained by constructing the apparatus so that the exposed substance receives practically all of the light given out. The temperature of the substance which is being investigated is at all times under the control of the operator.

The lamp consists of a transparent quartz tube, 70 cm. in length, closed at one end with a stopper of invar and inverted in a cistern containing pure mercury. The mercury cistern (*A*), Fig. 1, is closed at the top by a rubber stopper *B* through which the quartz tube passes. The air pressure in the cistern *A* may be varied by admitting or removing air through the side tube *C*. The height of the mercury column *D* varies with the air pressure in *A*. The quartz tube is of 7 mm. internal diameter, for the greater part of its length. It is enlarged at *E* to form an air-trap, also at *F* to form a condensation chamber, and again at *J* to form a reservoir for a mercury seal. The construction of the air-trap *E* will be understood from the drawing. Immediately above the air-trap is a water-jacket, *O*. Water circulating through this jacket serves to keep the positive electrode cool. This makes it possible to greatly increase the current density of the arc. The condensation-chamber *F* has at its lower end an internal flange which, together with the wall of the chamber, forms a pocket to hold a ring of mercury *G* which forms the negative electrode of the lamp. The wall of the tube is thickened at *H* and is ground to receive the conical end of the invar stopper *I*. This ground joint is sealed with mercury at *J*. The top of the quartz tube at *K* is constructed so as to fit closely about

¹ *J. Biochem.*, 20, 315 (1915).

drawn out from the body of the tube. The stopcock *C* is opened and as the quartz tube is evacuated, the mercury column *D* rises. The pumping is continued until the mercury column reaches and passes the ground joint at *H*. The stopper is then pressed down so that the joint is closed. The mercury which has passed above the joint serves as an air-tight seal.

The tube *C* is now connected with an aspirator and the air pressure in the cistern is reduced. The mercury column falls, leaving a Torricellian vacuum in the space below the invar stopper. In order to remove the last traces of air from the lamp it is necessary to boil the mercury column *D* during the first pumping, and in order to insure an air-tight seal at *H* the mercury in *J* must be boiled each time the seal is made. The occluded gases which are usually contained in the iron wire *N* and which are driven out during the first few "burning hours" of a new lamp, are removed from time to time by allowing the mercury column *D* to rise past the joint *H*. After these gases have been removed, the lamp seldom needs to be repumped. After pumping, the aspirator is disconnected from the invar stopper *I*, leaving the space above the mercury at *J* open to the outside air.

The invar stopper should not be heated while it is seated in the grinding at *H*. There is sufficient expansion of the invar at high temperatures to break the quartz. As long as the partial vacuum is maintained in the space above *J*, the stopper may be held up out of its seat without losing the mercury seal. The stopper is seated only when the lamp has cooled. It will be understood that the Bunsen flame may be turned directly on the quartz without fear of breaking. After heating the lamp is cooled immediately by a dash of cold water.

The lamp is operated on a direct current in series with a resistance, which, for voltages above 110, should be variable. It carries a current of from 12 to 15 amperes. The maximum length of arc obtainable is dependent upon the voltage of the line upon which the lamp is operated. With 110 volts on the line, an arc of about 9 inches can be maintained. With 220 volts, the lamp burns with an arc over 2 feet long. It is essential that the mercury column *D* be made the positive electrode; the lamp will not burn if the poles are reversed.

The solutions to be exposed to the light are contained in the triple-walled beaker *R*. The outside wall of the beaker is made of glass. The inside *S* is a screen for absorbing the heat rays. It is a double-walled quartz tube with the space between the walls open to the outside through the small tubes *U* and *V*. The heat rays are absorbed by a stream of water which passes between the walls of the tube. By adding various substances to the water, the double-walled quartz tube may be used as a selective light filter, or if desired, it may be used as a chamber in which to expose gases. The outside wall of the beaker is joined at *T* to the inner part by a rubber ring which forms the bottom of the beaker. Rubber

is very unstable under the action of ultraviolet light, and it would be better to have a ground joint at *T*, but the quartz tube used by the writer is too thin to stand grinding. The beaker has a capacity of 100 cc.

For measuring the temperature and stirring the solution during the exposure, a device is employed which is not shown in the drawing. It consists of a hollow gold wire (size No. 14 Brown and Sharp gage), bearing two rings of gold which encircle the inside wall of the beaker. The device is given a slow up-and-down motion by a crank on a driving motor. The upright hollow gold wire extends above the beaker and is open at the top, so as to receive one of a pair of thermal junctions made up of No. 32 "Ideal" and copper wires. The other (constant) junction is placed in water in a Dewar flask which is provided with a thermometer. The variable junction is pushed well down inside the hollow gold wire. The free ends of the copper wires are connected with a galvanometer which is sufficiently sensitive so that differences in the temperatures of the two junctions can be read to 0.1°.

The lamp is operated as follows: The line wire is disconnected from the invar stopper *I*. The beaker *R* is slipped off over the top of the lamp, and, if necessary, its outer and inner parts are separated at the joint *T*, so that the surface of the inner part *S* can be cleaned. The beaker and line wire are now replaced. The variable resistance is set so that when the lamp is short-circuited it will carry between one and two amperes. The stream of water is now started through the water-jacket *O*. Air is admitted into the cistern *A*, causing the mercury column *D* to rise until electrical contact is made with the electrode *G*. The air pressure in the cistern *A* is now reduced, and the mercury column falls, stretching out the arc between *D* and *G*. The variable resistance is now adjusted so that the lamp carries the desired number of amperes. The current may be varied from less than one ampere to the full carrying capacity of the lamp.

Connections are now made at *U* and *V*, water is allowed to flow through the space between the walls of the tube *S*, and the solutions to be exposed are placed in the beaker.

Fig. 2 is from a photograph of the lamp as installed in the Biophysical Laboratory of the Cancer Commission of the Harvard Medical School. The lamp is inclosed in a metal case made from a brass tube 6 inches in diameter. It passes through a hole in the table (the mercury cistern *A*, Fig. 1, resting on the shelf below) and is held in an upright position by a light framework which is attached to the case near the top. The brass tube, forming the case, is split longitudinally into halves which are hinged together along one side. One-half only is fixed to the table, the other movable half forming a door. The tube can thus be opened, making all parts of the lamp readily accessible.

As installed in this laboratory the lamp case is provided with a flue which passes up into the ventilator of the chemical hood. This flue is not necessary when the lamp is used in connection with the beaker described

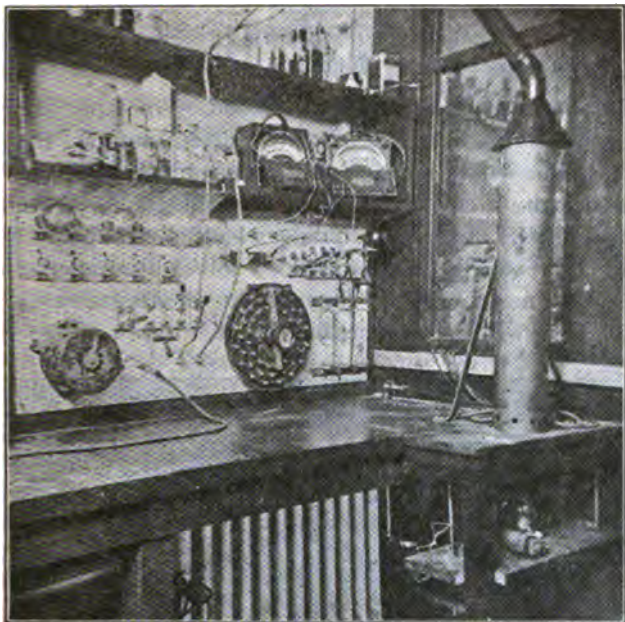


Fig. 2.

above. When used without the beaker, however, the ozone produced makes the laboratory a very unpleasant place in which to work, unless some means are provided for carrying the exposed air out of the room. The flue also disposes of a great deal of heat.

It is difficult to give an accurate description of the intensity of the light produced. Judging from the current density the light is much more intense than that produced by any lamp which has been previously described. Perhaps the following statement will serve to give an idea of the efficiency of the lamp in producing ultraviolet rays: It is known that egg-white is slowly coagulated by ultraviolet rays. In order to test the lamp, egg-white was diluted with water to make a 2% solution. The solution was brought to its isoelectric point and filtered clear; 100 cc. of the filtrate were placed in the beaker of the lamp, and the stream of water passing through the water-jacket was adjusted so that the solution of egg-white had a temperature of 16°. A flocculent coagulum began to appear 4 min. after the lamp was lighted. In this experiment the lamp was carrying a current of 11 amperes. (The amount of light probably varies as the square of the current density.)

It will readily be seen that the lamp is simple to operate and of great efficiency. It is hoped that it will prove to be of value in extending the use of ultraviolet light in biological and photochemical investigations.

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NOTES.

A Simple Stone-frame Chemical Hood.¹—In the equipment of three of the laboratory rooms recently fitted out at the Bureau of Standards, a somewhat novel type of chemical hood has been installed, the design of which is being considered for general use in the equipment of the chemical building which is now being planned for the Bureau. It is believed that this hood solves a number of difficulties which have been met by other chemists in so satisfactory a way that a description of it will be of general interest. Fig. 1 shows the general

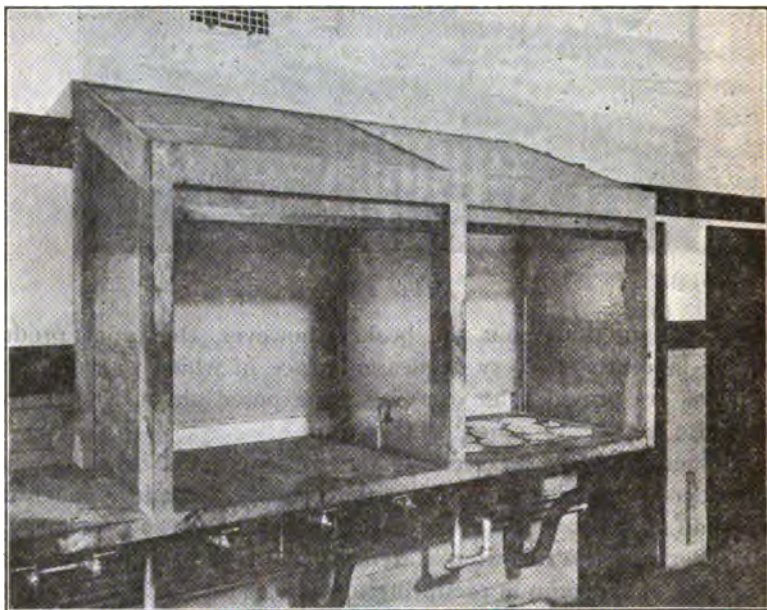


Fig. 1.

character of the simpler form of hood which has been used. This hood has the following advantages:

(1) It is simple, neat in appearance, of light weight, well lighted and, for a stone-frame hood, comparatively inexpensive.

(2) The inside of the hood, except the floor, is almost entirely of glass. There is no wood or metal at any point within the hood nor are there

¹ Published by permission of the Director of the Bureau of Standards.

any exposed joints of the stone frame; hence the hood is practically as resistant to chemical action as an all-glass vessel.

(3) There are no doors or other movable parts, hence no mechanism to break or get out of order. The hood is so designed as to give efficient ventilation when sufficient fan capacity is provided. The shape of the hood with low roof sloping to the front favors efficient ventilation, reduces to a minimum the surface upon which vapors condense in cold weather, and makes all parts of the hood, both inside and out, readily accessible for cleaning. For extreme conditions, where doors are required, the second form described below may be utilized.

(4) There are no horizontal surfaces within the hood upon which dust can collect and no edges from which condensed steam or acids are likely to drip or spatter into vessels within the hoods.

(5) A false back or baffle plate is provided which very effectively distributes the draft over the face of the hood and provides openings which can be adjusted for fumes both lighter and heavier than air. This baffle plate also prevents any dirt which falls or is blown down the flue from entering the hood and contaminating solutions.

(6) The glass, which forms the sides, partition, baffle plate, top, and front, slides into place after the frame is complete and requires no fastening. Any piece can, therefore, be removed for cleaning or can, if broken, be replaced in a few minutes.

For use in laboratories where a hood with doors is required, the design of the front of the hood shown in Figs. 1 and 2 is changed to that shown in Figs. 3-6. In this form, the horizontal stone strip across the front of the hood, which supports the front edge of the roof glass, is shaped as shown in section in Fig. 5, in order effectually to prevent dust from the roof sitting down inside the sliding door. Channel irons are attached to each side of the wooden sash of the doors and extended down through the base of the hood into the pipe supports. Chains attached to the lower ends of these channel irons run over pulleys just under the hood base to counterweights hung in any convenient manner

at the back of the hood. The counterweights may be placed inside of the rear pipe supports, if desired. By the use of this system, the doors are counterweighted by a mechanism that is entirely out of the way and almost entirely out of sight without the cost or waste of space made

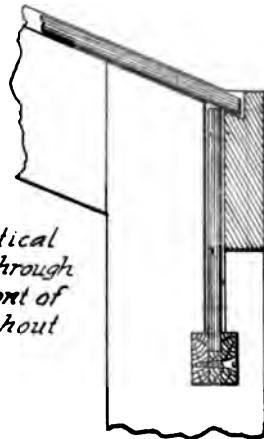
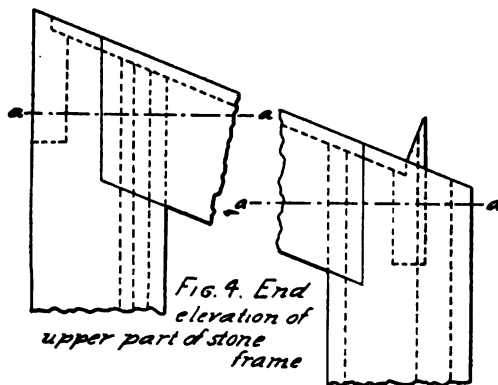
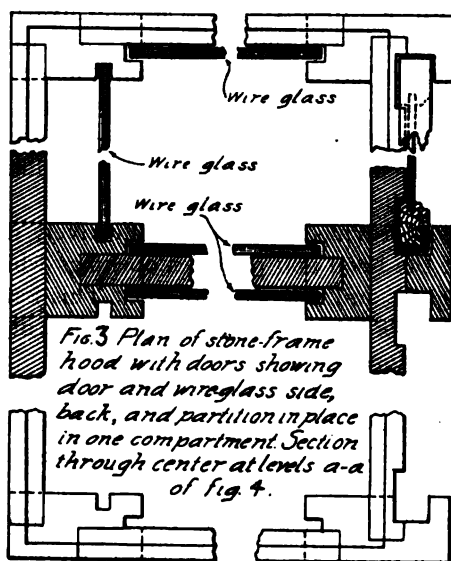


Fig. 2. Vertical section through top of front of hood without doors.

necessary by boxing-in, as is usually done in stone hoods, and without suspending the counter weights from any unsightly superstructure.

The frames of these hoods are fastened together with dowels inserted in holes drilled into the stone from the outside of the hood so that the dowel will not be attacked by acid fumes. The back of the hood is set directly against the wall, which is preferably covered with glass or glazed tile.



A separate vent through the wall may be placed for each compartment or a single vent may be made in the middle of the hood to draw equally from the two compartments. The height of the vent and the width of opening above and below the baffle plate determine the relative amount of air drawn from the top and bottom of the hood and may be varied to suit the character of the fumes which it will generally be desired to remove. In the hoods placed in this Bureau, openings of four inches and six inches are left, respectively, above and below the baffle plate.

The two-compartment hoods without doors have been in use for nearly two years and have given perfect satisfaction. Fumes of all densities are removed with equal facility; and with an efficient ventilating fan in operation no fumes from any part of the hood escape into the room.

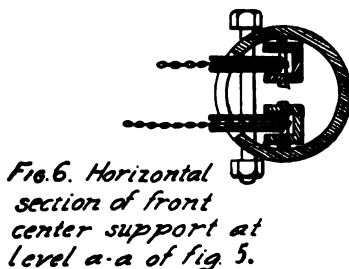
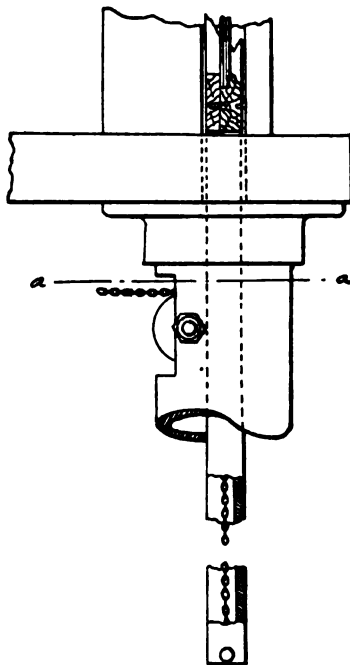
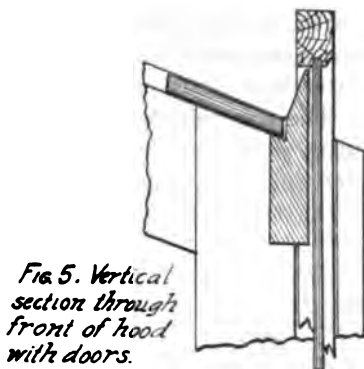
Anemometer tests were made to determine the volume of air required to give good ventilation. These tests were made in the front of the hood, both compartments of which were ventilated by a single duct, with only about one-third the normal front opening, the assumption being made that the reduction in front opening would not seriously affect the amount of air which would pass out through the comparatively small vent. It was found that about

two hundred cubic feet per minute passed through each compartment and that neither the total amount of air nor its distribution between the two compartments was materially changed by removing the baffle plate from one compartment. This volume of air would require a velocity of about thirty feet per minute over the full hood opening. Immediately following these tests, and with a full front opening, clouds of sulfur trioxide were liberated in various parts of the hood and were removed rapidly without contaminating the air of the laboratory. Many other similar trials have been made with clouds of smoke, ammonium chloride and bromine vapor. In every case the ventilation has been satisfactory.

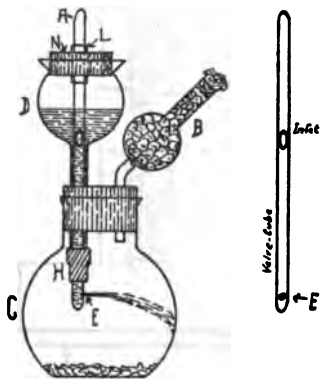
The ventilation is always much better in a compartment with the baffle plate in place than with the baffle plate removed. While the hoods have been in use, the amount of air passing through them has usually been considerably less than the volume noted in these tests. It seems evident from our experience with these hoods that no doors are needed for hoods of this type to insure adequate ventilation if efficient fan capacity is provided.

I wish to express by indebtedness to Mr. R. S. McBride for criticism and help in the design of these hoods and to Mr. C. A. Stutz and the members of the Chemical Building Committee of the Bureau of Standards for the tests made upon the hoods.

E. R. WEAVER.



A Simple Laboratory Apparatus for the Determination of Carbon Dioxide by Loss.—The following piece of apparatus was designed to meet the need, in this laboratory, of an apparatus of the Schrötter type. It is easily constructed, and is much simpler and less expensive than the Schrötter apparatus, and hence better adapted to general laboratory use. The acid inlet is more compact and efficient than that in any other similar simple apparatus. The action of the sliding valve-tube *A* absolutely prevents any escape of vapors except through the CaCl_2 tube *B*. The thin cork stopper *N*, with the glass tube *L*, the bore of which is only slightly greater than the diameter of the valve-tube, prevents any evaporation of acid in the thistle tube *D*.



Acid is placed in the thistle tube *D*, the cork stopper *N* is put in place and the apparatus is weighed. The sample is added to flask *C*, and the apparatus is again weighed. The valve-tube *A* is pushed down until the small opening *E* comes below the rubber tube *H*. When the desired amount of acid has been allowed to flow into the flask, the valve-tube *A* is raised, thus sealing the exit *E*. No CO_2 can escape except through

B. After reaction has ceased, the flask is gently heated for a short time, *A* is lowered and air is drawn through the apparatus to remove all CO_2 generated. The apparatus is allowed to cool, is weighed, and the percentage of carbon dioxide is calculated from the loss in weight.

As the apparatus was designed as a substitute for that of the Schrötter type it seemed best to run a series of parallel experiments with the two pieces of apparatus. Baker's c. p. BaCO_3 was used, charges of 0.5 g. BaCO_3 being employed, with 10 cc. HNO_3 (1 pt. con. acid to 1 pt. water).

The percentages obtained with the Schrötter apparatus were in all cases lower than the theoretical. The percentages obtained with the above apparatus were uniformly high. In the cases of both pieces of apparatus an accuracy of 0.1% was attainable, which for apparatus using this principle is sufficient.

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LABORATORY OF GENERAL CHEMISTRY,
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A Simple Buret Reader.—The author, while recently engaged in work involving many titrations, was led to investigate, incidentally, the different forms of buret readers available.

Various devices, including floats and lenses, were found to possess rather marked disadvantages. Floats are very limited in application

owing to the fact that they must be made to fit the buret perfectly if accurate results are to be obtained. Lenses are cumbersome and generally require holders of more or less elaborate construction.

The reader, shown in Fig. 1, was finally devised and found to be entirely satisfactory. It consists of a disk of ordinary mirror glass (*A*), about 35 mm. in diameter (shaped roughly with a pair of pincers, and the edges smoothed on a grind-stone), with the silvering scraped from a rectangular section (*C*), about 4×10 mm. A fine diamond-line (*a a'*) extends across the face, perpendicular to the long axis of the rectangle, as shown.

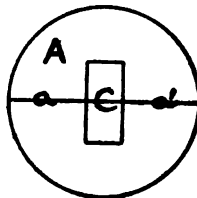


Fig. 1.

In use, the reader is held flat against the back of the buret so that the rectangle includes the meniscus; the diamond-line, in a horizontal position, being made to coincide with the graduation next below the meniscus. The reader is rotated somewhat, so that the reflections of the graduations are seen to one side. The eye is then moved up or down, the reader being also moved slightly, till the reflection of the graduation, on which the diamond-line is set, coincides with the diamond-line. In that position, the line of sight is normal to the buret, and parallax is avoided. As the

meniscus is always in very nearly the same position, relative to the transparent rectangle back of it, the lighting is constant and the meniscus always presents the same appearance, making accurate reading easy.

In Fig. 2 is shown, somewhat diagrammatically, the appearance of the reader in use. The diamond-line is shown at (*a a'*). The illumination is shown by the relative shading. The upper part of the rectangle is shown at (*C*) sharply defined, while the lower part (*C'*) is magnified by the solution

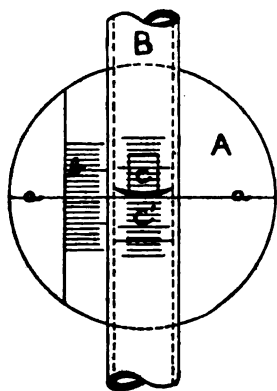


Fig. 2.

in the buret. The reflections of the graduations on the buret are shown at (*b*).

The advantages of this type of reader are the following:

1. Simplicity of construction.
2. Sharp, black and constant meniscus.
3. Elimination of errors due to parallax.

Obviously, this reader can be used with various types of calibrated tubes, besides burets, containing either solutions or mercury.

L. S. PRATT.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL,
AND THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY.]

THE ELECTRON CONCEPTION OF VALENCE. VII. THE THEORY OF ELECTROLYTIC DISSOCIATION AND CHEMICAL ACTION.

By K. GEORGE FALK AND J. M. NELSON.

Received April 26, 1915.

In the further development of the electron conception of valence,¹ a careful study of the relation which the phenomenon of electrolytic dissociation bears to this theory is of interest. Some of the simpler relations were pointed out in previous papers. The study of electrolytic dissociation in solution furnishes experimental methods for determining the distribution of some of the charges on some of the atoms of the molecules which show such ionization. These methods for locating the charges are confined to substances which conduct the electric current to a readily measurable extent in solution, and are, therefore, of limited value only for determining the charges on the atoms. The VI Paper of this series showed the importance of the solvent in ionization phenomena, a fact which had been emphasized by Werner, Walden and others.

The relation between the changes occurring in chemical reactions and the degree of electrolytic dissociation of one or more of the reacting substances will be taken up in this paper. For convenience of presentation, the conclusions reached in this study will be given at once and then some of the lines of evidence upon which these conclusions are based will be presented. *The changes occurring in chemical reactions do not depend upon the electrolytic dissociation of the reacting substances. The chemical changes are accompanied very often by electrolytic dissociation phenomena, but the latter parallel the former (or vice versa) and do not necessarily precede or cause them.*²

In the first place, it may be pointed out that the explanations of certain reactions, which at one time had been assumed to be purely ionic in character, have in recent years considered the un-ionized molecules as taking part in the reactions. Among those who have adopted this view may be mentioned Acree,³ Goldschmidt,⁴ Bredig,⁵ Snethlage,⁶ Dawson and

¹ For the earlier papers of this series cf. *School of Mines Quarterly*, 30, 179 (1909); *THIS JOURNAL*, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913); 36, 209 (1914); 37, 274 (1915); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 6, 212 (1912); *J. prakt. Chem. (N. F.)*, 88, 97 (1913); *Proc. Am. Phil. Soc.*, 53, 25 (1914).

² Similar views were brought forward by J. W. Walker (*J. Chem. Soc.*, 85, 1082 (1904)) in several papers on "Ionization and Chemical Action."

³ *Am. Chem. J.*, 37, 410 (1907); 49, 345 (1913).

⁴ *Z. physik. Chem.*, 81, 30 (1913).

⁵ *Ibid.*, 85, 170 (1913); *Z. Elektrochem.*, 20, 489 (1914).

⁶ *Z. physik. Chem.*, 85, 211 (1913).

Powis,¹ Taylor,² and Stieglitz.³ The theory of electrolytic dissociation does not postulate that only ions react.⁴ In fact, it has always been taken for granted by all except the most extreme followers of the theory of electrolytic dissociation, that reactions take place between un-ionized molecules.

In the second place, certain physical properties of substances, which, early in the history of the electrolytic dissociation theory, were considered to be dependent upon ionization have since been shown to be independent of it. Thus, the color of a salt in solution was assumed to be made up of the different colors of the ions and the un-ionized molecule. Later work showed that ionization changes do not affect the color of the substance. J. Lifschitz goes into these relations in some detail in a review entitled "Die Aenderungen der Lichtabsorption bei der Salz-bildung organischer Säuren."⁵ This fact will also be brought out more in detail with some organic substances (the indicators) where the color changes have been shown to be due to other reasons. The rotation of polarized light by salts has also been shown to be independent of the ionization.⁶

The explanations advanced at different times with regard to the color changes of indicators will serve to illustrate the views which are to be brought forward. Ostwald in 1894⁷ attributed the different color of an indicator in acid or alkaline solution to the different colors of the ions and un-ionized molecules. If the indicator substance itself was an acid, the color in acid solution would be that of the un-ionized molecule, while in alkaline solution the color would be that of the negative ion. If the indicator substance was a base, the color in alkaline solution would be that of the un-ionized molecule, in acid solution that of the positive ion.

This theory was shown not to be general enough to include the observed phenomena, and was replaced by the "chemical" theory first suggested (for phenolphthalein) by Bernthsen and developed by Stieglitz,⁸ who was the first to bring the chemical theory into harmony with Ostwald's theory of the sensitiveness of indicators, and especially by Hantzsch,⁹ who showed the ionic theory of indicators to be highly im-

¹ *J. Chem. Soc.*, 103, 2135 (1914).

² *Z. Elektrochem.*, 20, 201 (1914).

³ *THIS JOURNAL*, 35, 1774 (1913).

⁴ Cf. Arrhenius, *Z. physik. Chem.*, 2, 247 (1889).

⁵ "Sammlung chemischer und chemisch-technischer Vorträge," Vol. 21, Nos. 5-7 (1914); cf. p. 198 for the discussion with inorganic salts.

⁶ Cf. A. A. Noyes, "Congress of Arts and Sciences," Universal Exposition, St. Louis, 4, 322 (1904).

⁷ "Die wissenschaftlichen Grundlagen der analytischen Chemie," p. 104.

⁸ *THIS JOURNAL*, 25, 112 (1903).

⁹ *Ber.*, 39, 1090 (1906) and numerous articles since. Cf. also among others, Vorländer, *Lieb. Ann.*, 320, 116 (1902); *Ber.*, 36, 1485 (1903).

probable. The newer view considers every change in color of an organic substance to be due to an intramolecular rearrangement. Indicators form a special group in so far as the intramolecular rearrangements in their case are tautomeric in character and include, therefore, in most cases the shifting of a hydrogen atom in passing from one form to the other. The production of ions is secondary in the tautomeric changes, and if the ions are colored, it is because the un-ionized molecules from which they are derived are colored. The equilibrium between the tautomeric forms of a substance depends upon a variety of factors such as solvent, temperature, small amounts of certain added substances such as acids or bases, etc. To illustrate this, a few results obtained with ethyl acetoacetate may be quoted. The equilibrium between the tautomeric forms varies greatly in different solvents, the extreme values given by K. H. Meyer¹ being 0.4% enol form present in 3-5% aqueous solution at 0°, and 48% in hexane at 20°. Hantzsch² recently showed the important part played by solvents in affecting the equilibrium between the tautomeric forms of some indicators, and, therefore, the color changes of indicators. The action of acid and of alkali on the equilibrium between tautomeric forms is well known.³ Similar actions take place with indicators in aqueous solution, one form predominating in the presence of acids, the other (tautomer) in the presence of bases. In practical titrations, the indicator substance is present in such small concentration that the color change which accompanies the transformation of one tautomer into the other is very marked with the relatively small amount of added substance necessary to produce it.⁴ Other changes of conditions may be considered similarly for the indicators as a special class of tautomeric substances. In general, it may be stated that the various factors which influence the equilibrium between tautomers also influence the equilibrium between the different tautomeric forms of indicators, and that the question of the electrolytic dissociation of the indicator substances does not enter into the theory of their color changes as assumed in the earlier theory, although it appears to be connected with one of the factors involving the sensitiveness.

Esterification and saponification reactions are catalyzed by acids or bases. Until recently, the hydrogen or hydroxyl ions were assumed to be the catalysts, but the evidence brought forward recently showed that catalytic action by the un-ionized molecule must also be assumed. These reactions will now be taken up, but in order to develop the sub-

¹ *Ber.*, 45, 2843 (1912).

² *Z. Elektrochem.*, 20, 480 (1914); *Ber.*, 48, 158 (1915).

³ For example, cf. Hantzsch, *Ber.*, 43, 3052 (1910) for the action of alkalis on ethyl acetoacetate.

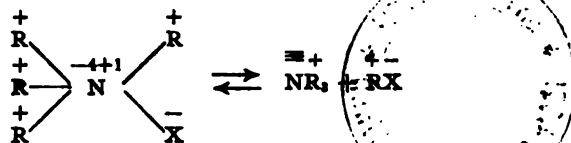
⁴ In this connection cf. A. A. Noyes, *THIS JOURNAL*, 32, 815 (1910).

ject logically, it will be necessary to describe a number of simpler reactions first. These reactions will be considered from the standpoint of the primary formation of addition compounds followed by their decomposition. Kekulé, in his textbook,¹ brought forward the view of primary addition followed by decomposition in organic reactions. Van't Hoff,² in 1878, came to similar conclusions with regard to some reactions which had been considered to be direct substitution reactions before. Michael has brought out much experimental work showing the same relations, and considers addition to play a greater part in reactions than has generally been assumed. Similarly, Emil Fischer³ stated recently,

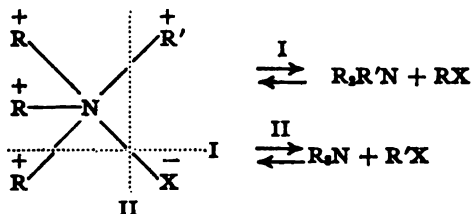
"... es bricht sich immer mehr die Ueberzeugung Bahn, das allgemein, auch bei gewöhnlichen Substitutionsvorgängen vorübergehende Additionen stattfinden, wie es schon Kekulé u. a. für wahrscheinlich erklärt haben."

A number of other workers might be quoted to the same effect.

It is well known that amines and alkyl halides combine to form substituted ammonium halides under certain conditions, and that under different conditions (rise in temperature, or addition of alkali) the latter decompose into amine and alkyl halide. An equilibrium exists in these reactions between amine, alkyl halide, and ammonium salt which may be represented by the formulas



The course taken by the reaction depends upon the equilibrium relation and whether any of the substances may be removed from the sphere of action. If more than one species of alkyl radical is present, the reaction may proceed in different ways as shown by the following equilibria:



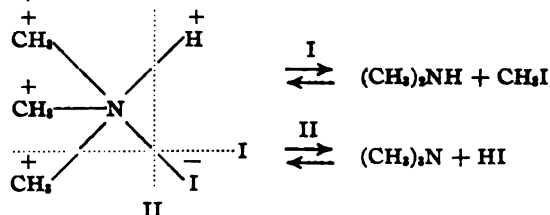
If more than two kinds of alkyl groups are present, the number of possibilities is increased correspondingly. In general terms, each of the positive groups is capable of uniting with the negative group, and there will be as many possible equilibria as there are different species of positive

¹ Vol. 1, 142 (1859).

² "Ansichten über die organische Chemie," 1, pp. 225, 244.

³ Ber., 40, 495 (1907).

groups. The fact that a number of possibilities exists, does not necessarily mean that all the reactions will occur to appreciable extents. The ones which will be observed are those for which the reactions proceed with the greatest velocities and where one or more of the products is removed from the sphere of action. As an example of the former, one of the reactions described by Wedekind¹ may be quoted: Benzylallyl-phenylmethyammonium iodide (prepared from allyl iodide and benzyl phenylmethyammine, or from benzyl iodide and allylphenylmethyammine, or from one of the other iodides and the corresponding amine) when heated alone or in aqueous solution formed benzyl iodide and allyl-phenylmethyammine, the halogen uniting with the radical containing the largest number of carbon atoms. To illustrate the latter, trimethylammonium iodide in the presence of alkali forms trimethylamine and hydrogen iodide, because the latter combines with the alkali.



The reaction proceeds to the right according to (II). An interesting reaction belonging to this type is that between cyanogen bromide and a tertiary amine in which addition takes place to form the trialkylcyanammonium bromide, which then decomposes into dialkylcyanamine and an alkyl bromide, the alkyl group of smallest molecular weight combining with the bromine.²

These reactions involve no electrolytic dissociation, but depend upon the formation of an onium compound of nitrogen. After being formed, these ammonium compounds may show electrolytic dissociation in suitable solvents, but this follows their formation.

This type of reaction forms the keynote of the reactions to be discussed, and it will be shown that it serves to correlate a number of apparently separate reactions, including esterification and saponification.³ That these reactions have not generally been considered from this point of view is doubtless due to the fact that the onium or salt-forming property of oxygen is not very marked, and the oxonium compounds are not as readily isolated under ordinary laboratory conditions as the corresponding nitrogen onium compounds.

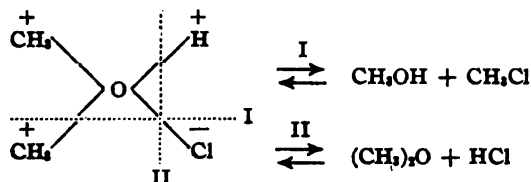
Some of the reactions of ethers are analogous to the reactions of the

¹ *Ber.*, **35**, 766 (1902); cf. Claus, *Ibid.*, **17**, 1324 (1884); **19**, 2785 (1886).

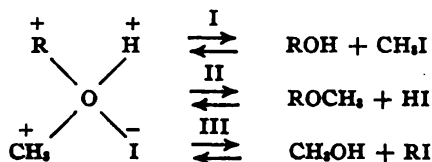
² J. v. Braun, *Ibid.*, **33**, 1438 (1900)

³ Cf. Henrich, "Theorien der organischen Chemie," p. 322 (1912).

amines just described. Dimethyl ether and hydrogen chloride at low temperatures readily form an oxonium salt, which decomposes at slightly higher temperatures.¹

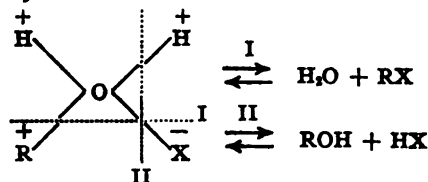


The equilibrium in the latter case follows (II). For reactions involving equilibria of a type similar to (I), it is only necessary to refer to the Zeisel method for determining methoxyl groups by heating the compound in question with hydrogen iodide. These reactions may be formulated as follows:



The substance ROCH_3 , when treated with an excess of hydrogen iodide will, according to the law of mass action, form the oxonium salt, which in turn will be in equilibrium with the substances represented in (I) and (III). The excess of hydrogen iodide in the reaction mixture will form water and methyl iodide from the methyl alcohol (in III) according to the next group of reactions to be described. The net result of the reaction will be the formation of methyl iodide according to Equations I and III, directly in the former, secondarily from the methyl alcohol in the latter, each molecule of methyl iodide corresponding to a methoxyl group present originally. The relative amounts of ROH and RI formed will depend upon the relative velocities of the reactions of Equations I and III, and also upon the conversion of ROH into RI by the hydrogen iodide (next group of reactions).

The group of reactions, similar to those just considered, except that a hydrogen atom is combined with the oxygen instead of a radical, will be considered next. This group of reactions, in which an alcohol and an acid interact, may be formulated as follows:

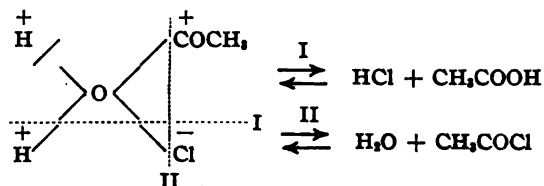


¹ Friedel, *Ber.*, 8, 548, 642, 777, 1193, 1348 (1875).

Addition of alcohol or HX , or removal of H_2O or RX would tend to make the reaction proceed to the right according to Equation II, the reverse conditions according to Equation I. The preparation of methyl chloride by passing HCl into a boiling solution of methyl alcohol in the presence of zinc chloride illustrates this reaction. HCl is continually added, CH_3Cl is removed by boiling, and H_2O by the zinc chloride.

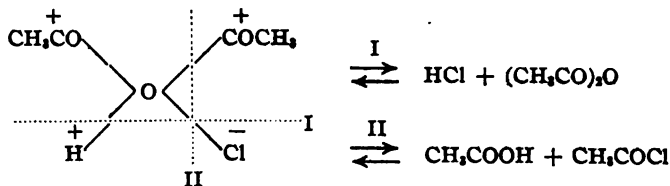
The formation of ethers from alcohols and other similar reactions may be explained by means of the equations already given. The course of the reaction is fixed in every case by the principle of mass action and the relative velocities of a number of possible reactions.

The next group of reactions which will be considered along the same lines contains in the formulas of the substances a group such as acetyl or benzoyl in place of a simple radical R . With acetyl chloride, for example, the following relations may be given:



The same products are formed by starting with acetic and hydrochloric acids. Removal of water and addition of HCl increases the amount of acid chloride formed.¹

If, in place of a second hydrocarbon radical (R) or of hydrogen, another acetyl group is introduced, the reactions may be formulated as follows:



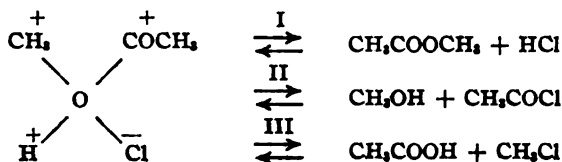
These reactions represent the customary method of preparation of acid anhydrides from acids (or their salts) and acid chlorides. An excess of acid is used and the HCl formed is driven off by heat. Both of these factors tend to increase the formation of the anhydride.

Similar formulations hold for all acetylations, whether of hydroxyl groups or of amino and imino groups. Two equilibria may be represented with the oxonium or ammonium compound taking part in both, and the factors involved in these equilibria determine according to the law of mass action which products will be formed in greater amounts. If the

¹ Cf. Friedel, *Compt. rend.*, 68, 1557; *Ber.*, 2, 80 (1869).

mass action effect does not enter into the question, owing to lack of excess of one or more of the constituents, or if it enters equally for two reactions, if a greater number is possible, then the relative velocities of the different reactions will determine the relative amounts of the substances formed.

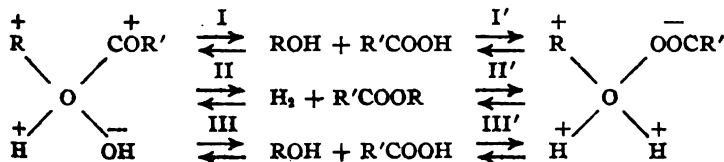
An interesting group of reactions is that in which one alkyl group and one acetyl group (for example) are involved, as follows:



This is evidently the group to which simple esterification and saponification may belong. Three equilibria are possible as indicated. With a large excess of alcohol, there would be a tendency for the substances represented by (I) and (III) to be formed. With primary and secondary alcohols the reaction has been found to proceed according to Equation I; on the other hand, with tertiary alcohols reaction III takes place with formation of alkyl halide. Also, if an ester such as ethyl acetate is heated with gaseous hydrogen halide, acetic acid and ethyl halide are formed. The velocity of this reaction is greatest with hydrogen iodide, smallest with hydrogen fluoride, decreasing with decrease in the atomic weight of the halogen.¹ In these last experiments, the reaction yielded the products shown by III because the hydrogen halide was present in excess. This group of reactions takes place if water is absent, or present in inappreciable quantities only.

In all of these reactions, in the equilibria between the oxonium compounds, and the possible products of the reactions only very small concentrations of the former need be assumed to be present at any time under ordinary conditions of working. They may therefore be considered to be intermediate products, the decomposition products being the substances actually obtained.

If alcohol and acid, or ester and water, are brought together, the following relations hold:



If the dissociation takes place according to (I), (I'), or (III), (III'), al-

¹ Sapper, *Ann.*, 211, 178 (1882).

cohol and acid are formed, if according to (II), (II'), water and ester.¹ Excess of alcohol or acid will increase the proportion of ester and water formed; removal of water increases the proportion of ester, etc. The equilibrium constants of the reaction between these substances will depend in each case upon the equilibria with the oxonium salt. The velocity of the reaction to form the oxonium salt and the velocity of the decomposition of the oxonium salt are small, as a rule. The addition of small amounts of HCl, H₂SO₄, or other acid increases the velocities of esterification and saponification greatly. These increases in velocity are connected with the ability or the velocity with which oxonium salts are formed.

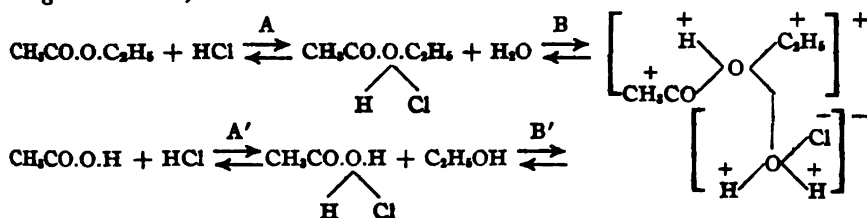
A better understanding of these relations may be obtained by first considering some simpler analogous reactions. Dry ammonium chloride, when heated, slowly dissociates into ammonia and hydrogen chloride.² When moist, very much more rapid dissociation takes place. In the latter case there is a partition of the HCl between the NH₃ and the water. If this is true of dissociation, it should also be true of combination. Dry HCl adds slowly to dry NH₃ to form an onium salt. It should also add slowly to H₂O. Ordinarily, however, water is made up of "double" and perhaps more complex molecules in which onium oxygen is already present; H₂O.OH, etc. A number of other facts, some of which will be given later, together with the experiments just indicated, suggest as a possible explanation of these phenomena that onium compounds react more rapidly than do the same constituents when not combined in the onium form. In other words, the positive and negative components of an onium compound add to some other atom, or atoms, in the onium manner, rapidly in comparison with the rate of addition of the same constituents when not combined in this way. The parallel phenomenon of electrolytic dissociation illustrates the same principle. Ammonium chloride ionizes instantaneously into NH₄⁺ and Cl⁻. It may also add in the onium manner as the same parts, to magnesium chloride, for example. One of these actions does not necessarily depend upon the other. Both depend upon a certain property of ammonium chloride. In the one case this property is measured by the electric current which the two parts (carrying opposite electric charges) are capable of transporting, in the other by the amount of the compound formed by the addition of the oppositely charged parts to a certain atom. Similarly, dry HCl adds slowly to dry NH₃; HCl reacts rapidly with water con-

¹ To this group belong the formation of tetramethylammonium salts of acetic and nitric acids (as well as betaines from the tertiary amine and ester); Willstätter and Kahn, *Ber.*, 35, 2757 (1902); Duvillier and Buisine, *Ann. chim. phys.*, [5] 23, 322, 331 (1881).

² H. B. Baker, *J. Chem. Soc.*, 65, 611 (1894); 73, 422 (1898).

sisting partly of double molecules containing oxonium combinations, and these oxonium chlorides then react rapidly with ammonia to form ammonium chloride. In brief, the catalytic action of the water may depend upon the presence of the oxygen in the onium form, which renders these compounds capable of reacting more rapidly to form other onium compounds.

The action of HCl as catalytic agent in esterification and saponification will now be taken up briefly. It is, of course, impossible to state with definiteness just what compounds are formed in a system as complex as the one under consideration. All that will be done is to give a series of reactions as a possible type of the course of the changes. These may readily be modified to conform to different experimental facts. The main purpose of the presentation is to call attention to the general principles underlying this type of reaction. The formulation for the reaction between ethyl acetate, water, acetic acid, ethyl alcohol, and hydrogen chloride, is as follows:¹



In the first place, it will be observed that in the reaction between ester or acid and HCl, the oxonium salt is considered to be formed with the hydroxyl oxygen. This agrees with the view of Goldschmidt. Experimental measurements do not offer a solution to the question whether the hydroxyl or the ketone oxygen is involved in the salt formation.² The hydroxyl or ether oxygen was chosen here in order to bring the reaction into line with the reactions described in the earlier parts of this paper. The ester or acid hydrochloride is an onium compound and, therefore, reacts rapidly to form a new onium compound by the addition of negative chlorine and positive complex to some atom capable of forming an onium combination, in this case the oxygen of the water or of the alcohol. In this way reactions B and B' form the substance indicated, containing two onium oxygen atoms.³ The brackets do not necessarily indicate electrolytic dissociation of the complex, although this is a possible accompaniment of the reaction, but are only intended

¹ An explanation of esterification similar to the one given here was suggested by Goldschmidt, *Z. physik. Chem.*, 70, 642 (1910); Goldschmidt and Thuesen, *Ibid.*, 81, 65-6 (1912).

² Stieglitz, *THIS JOURNAL*, 35, 1776 (1913).

³ For the experimental proof of the existence of ternary compounds of this type cf. Baumé and Pamfil, *J. chim. phys.*, 12, 260 (1914).

to show in the one case the negative group combined with the upper oxygen in the formula, in the other case the positive group combined with the lower oxygen. The concentration of this complex substance at any one time is undoubtedly small. This scheme accounts for the following facts: (1) The hydrogen chloride bears the same relation to the acid and to the ester. It, therefore, catalyzes the reaction in both directions. (2) The onium compound formation depends upon the strength of the acid catalyst. This is measured by the degree to which it breaks up in solution to form ions, a "physical" property similar to the "chemical" property of onium addition which controls the rate of reaction with water or alcohol. (3) Increasing the concentration of water favors the production of acid; increasing the concentration of alcohol favors the production of ester.

It is evident that the reactions might have been considered to take place between hydroxonium chloride and ester or between ethyl hydroxonium chloride and acid.¹ In this case also, an intermediate complex compound similar to the one given would be formed. Other schemes might be formulated, but the one given seems to fit in most satisfactorily with the simpler reactions and principles given before. It is evident also that the organic acid itself may catalyze the reaction by forming double molecules, which as oxonium compounds would react more rapidly with alcohol than the simple molecules.²

In considering the experimental evidence bearing upon the views outlined, it will be sufficient to indicate the large amount of material gathered in recent years regarding oxonium salts. A number of groups of organic substances containing oxygen have been shown to form salts with both organic and inorganic acids.³ The results indicate that both the nature and the strength of the acid and the character of the organic compound influence the readiness of formation and the stability of the

¹ Suggested by H. Goldschmidt, *Z. Elektrochem.*, 14, 581 (1908).

² Rosanoff, two years ago, presented the results of an experimental study of esterification (as a part of his general studies on catalysis, *THIS JOURNAL*, 35, 173 (1913)) by himself and his collaborators before the New York Section of the American Chemical Society. The reactions were found to follow the trimolecular law of reaction velocities closely, two molecules of acid and one of alcohol taking part, and any factors which increased the polymerization of the acid increased the velocity. Permission to communicate these facts here was granted by Professor Rosanoff, who expects to communicate the complete results very soon.

³ Among those who have worked in this field may be mentioned Collie and Tickle, *J. Chem. Soc.*, 75, 710 (1899); Collie, *Ibid.*, 85, 973 (1904); v. Baeyer and Villiger, *Ber.*, 34, 2679, 3615 (1901); 35, 1201 (1902); Hoogewerff and van Dorp, *Rec. trav. chim.*, 21, 353 (1902); Thiele and Strauss, *Ber.*, 36, 2375 (1903); Vorländer, *Ann.*, 341, 1 (1905); Plotnikow, *J. Russ. phys. chem. Ges.*, 36, 1088 (1904); 40, 64 (1908); Stobbe, *Ann.*, 370, 93 (1909); K. A. Hofmann, *Ber.*, 43, 178, 183, 2630 (1910); McIntosh, *THIS JOURNAL*, 32, 542 (1910); Maas and McIntosh, *Ibid.*, 34, 1273 (1912); 35, 535 (1913); Gomberg and Cone, *Ann.*, 376, 183 (1911); J. Kendall, *THIS JOURNAL*, 36, 1222, 1722 (1914); Kendall and Carpenter, *Ibid.*, 36, 2498 (1914); Kendall and Gibbons, *Ibid.*, 37, 150 (1915).

oxonium salts. The formation of oxonium salts need not be considered to be connected with the electrolytic dissociation. The readiness of formation of the oxonium salt often parallels the electrolytic dissociation in aqueous solution of the acid, but there is no direct evidence for such ionization in the mixtures studied. What is undoubtedly true is the fact that the properties of these acids are such that, when brought into aqueous solution under suitable conditions, electrolytic dissociation is observed, and when brought in contact with certain organic substances, possibly under different conditions, oxonium salts are formed. Furthermore, the oxonium salt itself may well ionize in solution.¹ On the other hand, while the formation of oxonium salts is not necessarily preceded by the electrolytic dissociation of any of the reacting substances, these same compounds might be formed by the suitable ions in solution reacting. Either the charged parts of un-ionized molecules may act, or ionized charged parts may act. Electrolytic dissociation is a special case of charged atoms, and the reaction is fundamentally the same.

It would be possible also to consider reactions such as sulfonation, nitration, aldol condensation, coupling, the Grignard, and probably others, in a similar way, but it is impossible to go into these in a paper such as this. Primary formation of addition compounds, followed by their decomposition in different ways as controlled by the law of mass action and the relative velocities of the different possible reactions form the basis of these views.

The theory of electrolytic dissociation has proven of greatest value in studying the reactions of inorganic chemistry, especially those taking place in aqueous solutions. An attempt to suggest a somewhat different point of view for these reactions will, naturally, meet with opposition, unless it can be shown that this new view not only retains all that is good of the old, but also brings out new relations, or explains, correlates, or accounts for reactions not satisfactorily dealt with on the older view. The latter considers that in aqueous (and also other) solutions, the ions of the substances present are the active factors in chemical reactions. The electron conception of valence considers that each atom in a molecule carries electric charges; the theory of electrolytic dissociation does not go beyond this, but on the other hand does not go as far and takes into account only some of the charges on the atoms of the molecules.

The point of view proposed here is that the ions in solution are formed from the substances, generally because of certain properties of the solvent, and also that due to certain, probably the same, properties of the solvent, the velocity of chemical change of the substances is increased. Both

¹ Cf. Walden, *Ber.*, 34, 4189 (1902); 35, 1764 (1903).

phenomena depend upon properties of the solvent but not upon each other. If the properties of the solvent affect both sets of reactions (the so-called chemical and physical) alike, there should be a perfect parallelism between the two sets of phenomena and one might then be considered to depend upon the other; otherwise this parallelism will not appear. For simple uni-univalent salts this parallelism apparently exists, and it is therefore not surprising that the "chemical" phenomena have been assumed to depend upon the "physical" phenomenon of electrolytic dissociation. For more complex salts, including the so-called double salts and many of the compounds included in Werner's classification, this parallelism does not exist and a number of hypotheses have been suggested to account for these deviations.

In the VI Paper of this series, it was shown that in the electrolytic dissociation of uni-univalent salts of the first order¹ onium combination with the solvent was a necessary preliminary. In the earlier part of this paper it was suggested on the basis of experimental facts, that onium compounds react more rapidly than do compounds not in onium combination. This may be the more fundamental phenomenon (onium compound formation by the solvent) upon which both electrolytic dissociation and reactivity depend. The fact that the electrolytic dissociation may be measured quantitatively in several different ways and that definite numerical values may be assigned to these degrees of ionization has resulted in this being considered the fundamental property and the chemical changes based upon them.

As stated before, there is no intention of suggesting that ions cannot react chemically. The broader view is proposed, namely, that every chemical reaction is one between charged atoms. Since ions form only a special case of charged atoms, they would be included. At the same time, many of the explanations of reactions which have heretofore been attributed to ions, may find a more rational explanation in other ways. This will now be illustrated by a group of reactions of inorganic chemistry.

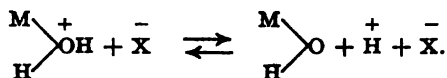
The theory of hydrolysis of Werner² and Pfeiffer³ may be combined with the views developed in this paper. They consider hydrolytic reactions to be dissociation reactions which may be formulated as follows: $RHX \rightleftharpoons R + HX$. In terms of the electrolytic dissociation theory, the equation would be written $RH + \overset{+}{X} \rightleftharpoons R + \overset{+}{H} + \overset{-}{X}$. The hydrolysis depends mainly upon the affinity of R and H for each other. A special case may be quoted from Werner. With metallic hydroxides, the hy-

¹ Werner "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," III edition, 1913, p. 89.

² "Neuere Anschauungen," pp. 232-237 (1913).

³ *Ber.*, 40, 4036 (1907).

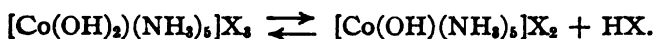
drolytic dissociation may be represented by the equation



The aquo-metal ammines react in this way. For instance, the electrolytic dissociation of aquopentamminecobalti salts in aqueous solution would be represented by the equilibrium



while the hydrolysis would be represented by the equilibrium



Just how much to the right this reaction proceeds will depend upon the equilibrium relationships and upon the concentrations of the substances. If one of the substances is removed from the sphere of action, as for instance HX by the action of a base, more of the product of hydrolysis, in this case hydroxopentamminecobalti salt, will be formed. The general formulation is as follows:



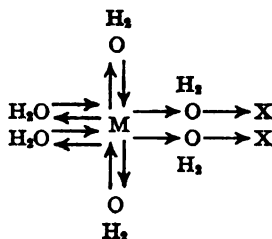
The reactions between some metallic salts, ammonium salts, and ammonia in aqueous solution will be considered now. Many of the bivalent metals such as nickel, magnesium, etc., form hydroxides insoluble in water but soluble in solutions of ammonium salts. The generally accepted explanation for the solubility in solutions of ammonium salts or for the nonprecipitation by ammonia, if ammonium salts are present, is that the ammonium ion of the ammonium salts drives back (or represses) the electrolytic dissociation of the ammonium hydroxide so that the hydroxide ion is not present in sufficient concentration to exceed with the metal ion the solubility product of the metal hydroxide.¹ The explanation of these reactions which will be developed here depends upon the hydrolysis reactions and equilibria outlined and upon the structures of salts in solution developed in the VI Paper.

A bivalent metal halide, MX_2 , will be chosen as example. In water

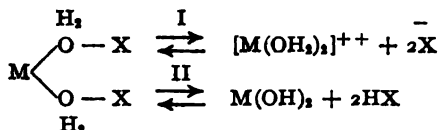
solution the compound $\begin{array}{c} \text{H}_2 \\ \diagup \\ \text{O}-\text{X} \\ \diagdown \\ \text{O}-\text{X} \\ \diagup \\ \text{H}_2 \end{array} \text{M}$ will be present and negative X com-

bined with O carrying a predominatingly negative charge will ionize into $[\text{M}(\text{OH}_2)_2]^{++}$ and $2\bar{\text{X}}$. It is probable that a substance of this sort will take up more (generally four) molecules of water in onium combination with the metal element. The complete formula may be written

¹ Cf. Loven, *Z. anorg. Chem.*, 11, 404 (1896); Herz and Muks, *Ibid.*, 38, 138 (1904).



Since the last four H_2O molecules are not directly involved in the theoretical views to be developed, the formulas will be written without them. The substance $\text{M}(\text{OH})_2\text{X}_2$ may undergo hydrolytic dissociation as shown in Equilibrium II.

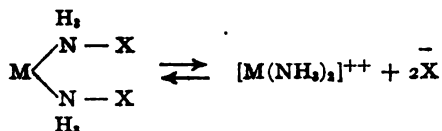


The reaction which will be observed depends upon the equilibria (affinity relationships) of (I)¹ and (II) and upon the addition or removal of any of the products. For instance, Equilibrium II will proceed to the right if a base is added. The addition of the base removes HX and causes more $\text{M}(\text{OH})_2\text{X}_2$ to undergo hydrolysis until ultimately only $\text{M}(\text{OH})_2$ will be present. This reaction will take place especially if $\text{M}(\text{OH})_2$ is insoluble, but it is important to note from these equations that it is due to the removal of HX by the base rather than direct metathesis. The simplest way of looking at the change, if only the initial and final substances and their formulas are used, is $\text{MX}_2 + 2\text{M}'\text{OH} = \text{M}(\text{OH})_2 + 2\text{M}'\text{X}$; but this, for one thing, leaves out of account the action of the solvent. Written in the ionic form $\text{M}^{++} + 2\text{OH}^- = \text{M}(\text{OH})_2$, while apparently going back to more fundamental relationships, does not show what direct part, if any, the solvent plays. By means of the equilibrium reactions as formulated, the part the solvent plays is made evident. Furthermore this reaction is brought into line with a great number of others (a number of which were given in the earlier part of this paper), and also shown to belong to the group of hydrolytic reactions, to which the theoretical explanations developed by Werner apply.

Ammonia has been shown to be analogous to water in its reactions. Onium compounds are formed to a greater or more readily observable extent with it than with water. If ammonia is added to a solution of MX_2 , it is evident that a compound $(\text{H}_3\text{N} \rightleftharpoons)_4\text{M}(\rightarrow \text{NH}_3 \rightarrow)_2\text{X}_2$, or (omitting the four ammonias in onium combination with M) $\text{M}(\text{NH}_3)_2\text{X}_2$, may be formed. The relative amounts of $\text{M}(\text{OH})_2\text{X}_2$

¹ The "intermediate" ion is not given in this equilibrium, but doubtless is present.

and of $M(\text{NH}_3)_2\text{X}_2$ which will be formed, or the distribution of MX_2 between water and ammonia, will depend upon the relative stabilities of these compounds under the given conditions. The substance $M(\text{NH}_3)_2\text{X}_2$ undergoes electrolytic dissociation as follows:¹



Ammonolytic dissociation to form $M(\text{NH}_3)_2$ and HX , analogous to the hydrolysis of the hydrated salt, does not seem to occur with these compounds under these conditions.² The addition of a base has, therefore, no direct action on a substance of this formula in the way of influencing the equilibrium. Beyond the possibility of a direct metathetical reaction, the base plays no part, as it does in the hydrated salt, even if the hydroxide is not soluble. To sum up, the possible reaction between a base and a substance MX_2 in water in the presence of ammonium salts or ammonia will depend upon the relative amounts of hydrated and ammoniated salt present; if an appreciable amount of the former is present, $M(\text{OH})_2$ may be precipitated; if the salt is entirely present as the latter, no $M(\text{OH})_2$ will be precipitated.

Ephraim³ recently published some very careful studies on the stability of the metal ammoniates. He determined the temperatures at which the hexa-ammonia (and substituted ammonia) derivatives of a number of salts of the bivalent metals (including Be, Ni, Co, Fe, Cu, Mn, Zn, Cd, Mg) showed definite vapor pressures. The results give a measure of the relative stabilities of these compounds, and consequently also for solutions of them. This gives no direct evidence as to the distribution of any given salt between water and ammonia with both present in solution, but does give a relative measure of the amounts of the ammoniates formed by a number of different salts. For instance, the salt $\text{NiCl}_2 \cdot 6\text{NH}_3$ shows a vapor pressure of 500 mm. at 130° , while the salt $\text{MgCl}_2 \cdot 6\text{NH}_3$ shows the same vapor pressure at 24.5° . This means that a very much smaller concentration of ammonia would be needed in solution to form the hexa-ammoniate with a nickel salt than would be necessary for a magnesium salt. Consequently, as a result of the distribution of the salt between the ammonia and the water, the concentration of ammonium salt needed to prevent the precipitation of the metal hydroxide if a base is added would be much less for the nickel salt than for the

¹ Possible intermediate ions are omitted.

² Perhaps the mercury ammonia compounds dissociate in this way under suitable conditions.

³ *Ber.*, 45, 1322 (1912); 46, 3103, 3742 (1913); 47, 1828 (1914); 48, 41 (1915); *Z. physik. Chem.*, 81, 513, 539; 83, 196 (1913).

magnesium. The salts studied by Ephraim may be arranged in a series showing the relative amounts of ammonium salts needed to prevent precipitation if a base is added. This explanation of the action of ammonium salts in preventing the precipitation of the hydroxides of bivalent metals is advanced in place of the usual theory of repression of the electrolytic dissociation of ammonium hydroxide by ammonium salts, as bringing the reactions into line with other equilibrium reactions, and as considering the solvent (including thereby dissolved substances) as the predominating influence in the reaction. These reactions are now being studied quantitatively from this point of view and the results will be communicated later.

It is evidently possible to apply similar views to other reactions. No more will be taken up here in detail, but only the view will be emphasized that chemical reactions need not be considered to depend upon electrolytic dissociation. With the atoms in a molecule all carrying electric charges, certain properties of a solvent make some of these charges evident to experimental methods, while certain, perhaps very often the same, properties of the solvent increase the extent or rate of a reaction. These phenomena are independent of each other but both dependent upon the solvent, or possibly some other underlying cause. Many of the changes which have been considered heretofore as metatheses involve, without doubt, primary addition and subsequent decomposition or splitting off in various ways of the reacting molecules.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE MELLON INSTITUTE, UNIVERSITY OF PITTSBURGH.]

USE OF IODINE AS A DEHYDRATING AND CONDENSING AGENT.

BY HAROLD HIBBERT.

Received May 3, 1915.

The question of devising some simple general method for the dehydration of organic hydroxy compounds has recently (on account of its importance in connection with the rubber synthesis) been made the subject of considerable activity among chemical investigators, as is indicated by the numerous patents taken out on this subject. In the interesting communication of Kyriakides¹ on the "Preparation of Butadiene—1 : 3 Hydrocarbons," some valuable data are quoted to show that the dehydration of various glycols and alcohols can be readily brought about in the "wet way" by heating them with a small amount of a mineral acid of high dissociating power. It would seem that the use of such a reagent offers many advantages over that of such substances as sulfuric acid,² potassium

¹ THIS JOURNAL, 36, 980, 987 (1914).

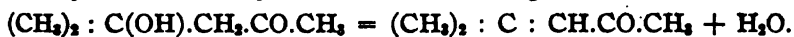
² The use of phosphoric acid for the preparation of unsaturated derivatives (Newth, *J. Chem. Soc.*, 79, 917 (1901)), has so many advantages over sulfuric acid that it is difficult to understand why this reagent is not more frequently employed.

bisulfate, oxalic acid, zinc chloride, aluminum chloride, etc., since the formation of by-products is thereby almost entirely avoided. This author explains the dehydrating action of such acids as being due to a primary ester formation followed by a subsequent dissociation of this into halogen acid and unsaturated derivative. A very small amount of mineral acid suffices in this way for the dehydration of a large amount of the carbinol or glycol, respectively. Of considerable interest is the fact that the salts of these acids with weak bases are also equally efficient in bringing about such decompositions. Due to the stable character of the halide esters derived from primary alcohols, the method was found to be inapplicable to these compounds.

Some two years ago it was found by the writer that the marked disadvantages associated with the majority of such condensing agents could be avoided, and highly satisfactory yields of unsaturated derivatives obtained, by heating the hydroxy compound with a minute quantity of iodine. Thus diacetone alcohol when heated alone under ordinary pressure boils around 164° , though with considerable decomposition, acetone being formed.



When mixed, however, with as small a quantity as 1/10,000 part of iodine, and then distilled, it breaks down into water and mesityl oxide, practically a theoretical yield of the latter being obtained.



The reaction has, in fact, been found to be capable of general application. Further, in presence of a small amount of iodine, tertiary amyl alcohol on heating yields amylene; pinacone is converted into dimethylbutadiene, and cyclohexanol into tetrahydrobenzene. Under the influence of the same reagent, glycols yield polyglycols; glycerol is transformed into polyglycerols and condensation between aldehydes and glycols is readily brought about.¹

Theory of the Process.

It is of interest that the ease of decomposition is found to vary in a marked manner with the nature of the alcohol employed. Thus while tertiary alcohols, on heating with small amounts of iodine, lose water very readily, this decomposition takes place, in general, much more slowly with the secondary, and scarcely at all with the primary derivatives. On the one hand, tertiary amyl alcohol (ethyl dimethylcarbinol), pinacone, and diacetone alcohol all decompose with the greatest ease into water

¹ Recent experimental work carried out at this Institute by my colleague Benjamin T. Brooks has shown that the reaction is also applicable to a variety of dehydration phenomena in the terpene series. This data will appear in a forthcoming issue of *THIS JOURNAL*.—H

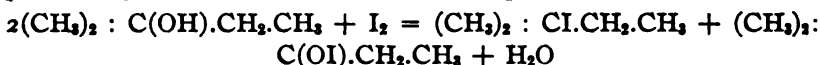
and unsaturated derivative, while with a secondary alcohol such as cyclohexanol the formation of tetrahydrobenzene takes place very slowly.

How are we to explain the remarkable effect produced by such small amounts of iodine?

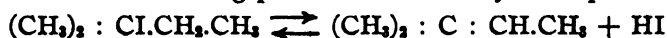
If we call to mind the fact that the action of iodine on a metallic hydroxide results in the primary formation of an iodide and hypoiodite



and assume that organic (alkyl) hydroxides (in other words, alcohols) may possibly function in a similar manner, then in the case of dimethylethylcarbinol mentioned above, this in presence of iodine, might also be expected to yield a mixture of iodide and hypoiodite:



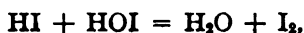
Now it is a well-known fact that the majority of alkyl halides dissociate to a greater or less extent at or below their boiling point, and of these the iodides represent the most unstable derivatives. Thus, in the case of all alkyl iodides we have at least a partial decomposition¹ on heating into olefine and hydriodic acid, so that with the iodide in question we should have some dissociation taking place as indicated by the equation:



and presumably the hypoiodite, being much more unstable would dissociate even more readily.



The interaction of the two acids HI and HOI would, however, give water and iodine,

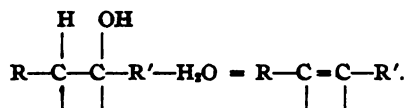


the latter then reacting again as shown in Equation 1. In this way we have a continuous cycle of reactions (in which the iodine functions as a catalytic agent), resulting in the formation of two final products, *vis.*, water and the unsaturated derivative. It would seem that the reactions just outlined are capable of being applied to any tertiary, secondary or primary alcohol, and the theory apparently offers a simple explanation of the part played by the iodine in reactions of allied types. Since, in general, the stability of the alkyl iodide and hypoiodite increases from the tertiary through the secondary to the primary derivative, it is to be expected that the iodine will function more readily with tertiary alcohols of the type of pinacol than with secondary, such as cyclohexanol, and this in fact has been found to be the case. The method is apparently inapplicable to the primary alcohols on account of the much more stable character of the corresponding alkyl iodides.

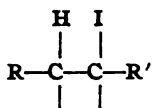
¹ It is scarcely necessary to point out that a *partial* decomposition is all that is required by the theory under discussion.

In general, it may be said, that the presence of iodine should facilitate the splitting off of water from any organic compound in which one of two adjacent carbon atoms has a hydroxyl (OH) group, the other, a hydrogen atom attached to it.

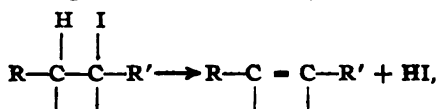
Written in a general form this would be indicated by



Further, according to this theory, the ease of splitting off of the water should be dependent on the ease with which the iodide



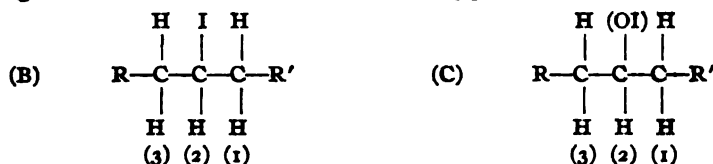
is capable of dissociating into unsaturated hydrocarbon and HI



which in turn is dependent on the greater or less labile nature of the H atom. Thus it may be assumed that an alcohol of the type



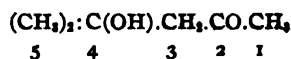
would give with iodine the iodide (B) and hypoiodite (C).



and whether hydrogen would split off from carbon atom (1) or (3) would depend on the relative affinity between it and the respective carbon atom. If this were the same, or approximately the same, we should expect to get from the alcohol (A) equal quantities of the two isomers (D) and (E).



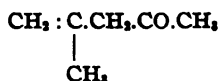
In the case of diacetone alcohol



we should expect that the presence of the negative carbonyl group would render the hydrogen atoms attached to carbon atom (3) more labile than those attached to carbon atom (5) so that mesityl oxide



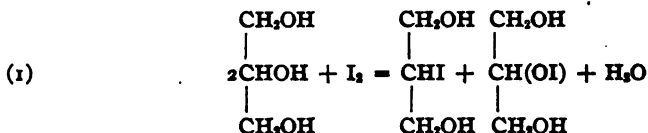
and little or none of the isomer



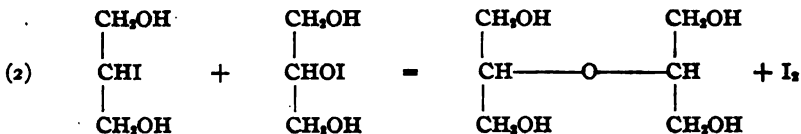
should be obtained.

The behavior, however, on redistillation (p. 1756) of the anhydrous distillate obtained by heating diacetone alcohol with a small quantity of iodine seems to indicate the presence of some of this second derivative.

While the above theory would thus appear to offer a good working hypothesis, it is quite possible that the alkyl iodide and hypiodite react *directly* without undergoing a previous dissociation, and such a view would seem to offer a ready explanation of the action of iodine in bringing about the condensation of glycols to polyglycols and of glycerol to polyglycerol. Since, as indicated above, a secondary alcohol is more reactive than a primary, presumably on heating glycerol with iodine, the secondary alcohol group will be the one to react, with the formation of an iodide and hypiodite.



In presence of the two negative hydroxyl groups it seems possible that the iodide and hypiodite might function exactly as HI and HOI, respectively, and thus react directly to give oxide and free iodine



the iodine then reacting again as in Equation 1.

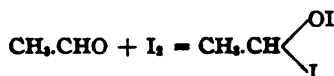
It is of interest that, as shown by Kyriakides,¹ the action of small amounts of strongly dissociating acids such as HCl, HBr, HI on glycols results in the formation of unsaturated alcohols or hydrocarbons, or both, depending on the conditions employed, while when iodine is employed as the dehydrating agent the principal product, as shown later, is a polyglycol, although undoubtedly some of the unsaturated alcohol is also obtained.² This would seem to indicate that in the case of these substances

¹ *Loc cit.*

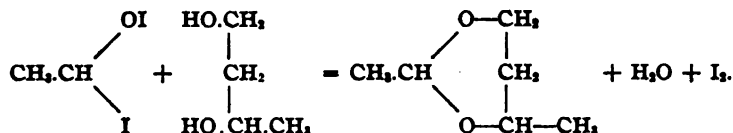
This point is to be investigated later.

a *direct* decomposition between the alkyl iodide and hypoiodite takes place as indicated above, and would seem to provide evidence for the assumption that, in the cases where iodine is employed as the condensing agent, both types of reaction may take place depending on the nature of the compound in question.

In the condensation of glycols with aldehydes, for example, of butylene glycol with acetaldehyde, an apparently simple explanation of the manner in which the iodine functions would seem to lie in the assumption of the primary formation of an addition compound of the aldehyde and iodine



and that this then reacts with butylene glycol to give 1-methylpropane-diol-ethylal, water and iodine



If the above theory is correct, then since the iodine plays the part of a *direct* catalyzer (cf. Rosanoff, "Outline of a Theory of Homogeneous Catalysis"),¹ in all such reactions it should obey "the law of mass action." Some indication that this is the case is obtained from the experiments on the condensation of glycerol (pp. 1760-1761), and further work is being undertaken to confirm this view.

Experimental Part.

This has been divided so as to embrace the following groups:

- I. Synthesis of unsaturated hydrocarbons from alcohols.
- II. Synthesis of unsaturated ketones from ketone alcohols.
- III. Synthesis of unsaturated aldehydes from aldols.
- IV. Synthesis of polyglycols and polyglycerols.
- V. Condensation of glycols with aldehydes.

Group I.—Synthesis of Unsaturated Hydrocarbons from Alcohols.

(a) **Preparation of Trimethylethylene from Tertiary Amyl Alcohol.**—Sixty grams of tertiary amyl alcohol ($\text{C}_2\text{H}_5\cdot\text{C}(\text{OH}) : (\text{CH}_3)_2$), b. p. 101-102°, were mixed with 0.14 g. of iodine and the product heated on the steam bath for about 24 hours, using a distilling flask and glass beads, the side tube of the flask being connected with a reflux condenser. There was a steady decomposition of the alcohol into the corresponding amylene (trimethylethylene). The distillate, after drying with calcium chloride, was redistilled and yielded about 27 g. of a product, b. p. 35-39° (principally 36-37°). Trimethylethylene, $\text{CH}_3\text{CH} : \text{C} : (\text{CH}_3)_2$, boils at 39°.

¹ THIS JOURNAL, 35, 173 (1913).

The residue in the flask consisted of the unchanged tertiary amyl alcohol.

(b) **Synthesis of Dimethyl Butadiene from Pinacone.**—A small quantity of pinacone was prepared by reducing acetone with magnesium amalgam, according to the method of Hollemann.¹ On completion of the reaction the product was distilled with steam and the pinacone hydrate obtained in solid form by cooling the aqueous distillate to around 0°. This was dehydrated by leaving over night in a vacuum desiccator over sulfuric acid, during which period considerable volatilization took place, 9 g. of the hydrate yielding only 5 g. of pinacone.

Preparation of Dimethyl Butadiene.—Five grams of pinacone were transferred to a small flask, mixed with 0.012 g. iodine, and distilled slowly over the naked flame, using a fractionating column. A rapid decomposition took place when the temperature of the outer bath reached 140°. The product distilling over (weight approximately 3 g.) was dimethyl butadiene, which on redistillation boiled at 69–72°. (According to the literature, dimethyl butadiene boils at 69.5°.) It combined with bromine with great readiness, yielding a crystalline tetrabromide melting around 135°.

Several attempts were made to prepare dimethyl butadiene from pinacone hydrate by heating this product with small traces of iodine, but only poor yields of the unsaturated hydrocarbon were obtained. Thus, while pinacone itself, in presence of a relatively small amount of iodine, goes over very readily on heating into dimethyl butadiene, the presence of water, in the form of the hydrate, seems to prevent this reaction from proceeding except to a limited degree, and it was invariably found that pinacone distilled over with the water, recombining in the distillate to form pinacone hydrate.

(c) **Preparation of Tetrahydrobenzene from Cyclohexanol.**—Twenty-seven grams of cyclohexanol were mixed with one-fiftieth its weight of iodine, and the product heated in a distilling flask (the neck of which was filled with glass beads to serve as a fractionating column) to about 170–175° for about 60 hours. The distillate (amounting to 21 g.) separated into two layers. After removal of the lower aqueous portion and drying the upper layer with calcium chloride, about 18 g. remained, from which, on a subsequent fractionation under ordinary pressure, about 7–8 g. of pure tetrahydrobenzene, b. p. 82–84° were isolated.

The method is of interest in view of the fact that a patent on the preparation of synthetic rubber substitutes, by passing the vapors of cyclohexanol over heated platinum or other contact material, has been taken out by the Badische Company.

Possibly the above process could be utilized for the preparation of tetrahydrobenzene on the commercial scale, and it would seem that better

¹ *Rec. trav. chim.*, 25, 206 (1906).

yields of the unsaturated rubber hydrocarbons should be obtained from this, than by the use of cyclohexanol itself.

Group II.—Synthesis of Unsaturated Ketones from Ketone-Alcohols.

Preparation of Mesityl Oxide from Diacetone Alcohol.—It was stated in the introduction that diacetone alcohol, when distilled under ordinary pressure, boils around 164° , undergoing, however, considerable decomposition into acetone. In presence of a small quantity of iodine, the reaction proceeds in an entirely different manner, mesityl oxide being obtained in a practically quantitative yield.

Expt. I.—700 g. of diacetone alcohol were mixed with 0.5 g. of iodine (= 0.07%) and the product distilled under atmospheric pressure over the naked flame, using a short fractionating column filled with glass beads. The thermometer in the column indicated a temperature of 90° after the first few drops had distilled over, and remained there until about one-third the distillate had been collected. After about two-thirds had distilled over the remaining distillate was collected separately and found to be free from water, consisting in fact of practically pure mesityl oxide, b. p. $125\text{--}130^{\circ}$ (principally $128\text{--}130^{\circ}$). The remaining two-thirds of the distillate consisted of two layers, and after removing the lower aqueous portion, the upper layer was dried with calcium chloride and refractioned.

Fraction 1.	B. p. 60° to 80°	6 g.
Fraction 2.	B. p. 80° to 125°	47 g.
Fraction 3.	B. p. 128° to 130°	259 g.

312 g.

The aqueous layer, after being saturated with potassium carbonate, yielded 11 g. of an oil consisting of equal parts of acetone and mesityl oxide. The total yield of mesityl oxide (consisting of everything boiling between 80° and 130°) was 578 g., representing a yield of 97.8% crude mesityl oxide.

Expt. II.—A further experiment was carried out using 200 g. of diacetone alcohol and 0.02 g. iodine (representing 0.01% or 1 part in 10,000) and in this case also practically a theoretical yield of mesityl oxide was obtained.

It then seemed of interest to determine whether the method is applicable to mixtures of diacetone alcohol and acetone. Using the above quantity of iodine (*viz.*, 0.01 to 0.02% calculated on the weight of diacetone alcohol present) it was found that on distillation the greater part of the acetone distilled over below 80° , the further distillation then resulting in the decomposition of the diacetone alcohol into mesityl oxide and water which proceeded exactly as indicated in the above experiments.

In every case a few cc. of a dark-colored oil remained in the flask, which however, did not give any reaction indicating the presence of free iodine.

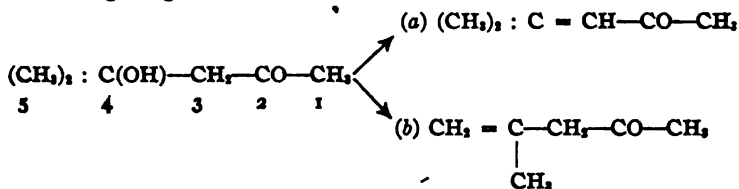
It was thought that possibly the presence of this product would suffice to bring about the catalytic decomposition of a fresh quantity of diacetone alcohol, without the further addition of iodine, but on carrying out such an experiment by introducing a fresh quantity of diacetone alcohol and distilling, little or no decomposition into mesityl oxide occurred.

The mesityl oxide as thus obtained is a clear, colorless product and quite free from diacetone alcohol as shown by the following experiment:

100 g. of the product, b. p. 120° to 130° , were shaken four times, using 20 cc. of water for each operation and the remaining oil dried with calcium chloride and redistilled. There were obtained 95.7 g. of mesityl oxide, b. p. 120 – 130° .

From the boiling point, physical properties, etc., there is no doubt that the method gives a practically pure product and thus represents an especially simple and inexpensive process.

It was pointed out in the previous discussion that the decomposition of diacetone alcohol might very well proceed simultaneously in two directions, thus giving rise to two isomeric substances:



Owing, however, to the proximity of the carbonyl group it was thought that the hydrogen atoms attached to carbon atom (3) would prove to be much more labile than those attached to carbon atom (5) so that relatively little of (B) would be formed. Curiously enough it was found that a quantity of a lower boiling product (b. p. 80 – 125°) was always obtained. After carefully drying this product and submitting it to a re-distillation the boiling point invariably rose with each successive re-fractionation, so that eventually it was completely converted into mesityl oxide, as indicated in the following typical experiment:

Six hundred grams diacetone alcohol were mixed with 0.2 g. iodine, and the mixture distilled over the naked flame at ordinary pressure, using a fractionating column and glass beads.

Fraction (1). ¹	70–125°	370.4 g.
Fraction (2).	125–130°	144.3 g.
Fraction (3).	130–131°	28.1 g.
		<hr/>
		542.8 g.

(These temperatures are those indicated on the thermometer in the neck of the distilling flask.)

¹ No record was kept of the amount distilling over below 70° and of the residue left in the flask.

Treatment of Fraction I (B. P. 70-125°).

After separating off the water, the product was shaken four times with water (50 cc. for each operation) in order to remove any acetone and diacetone alcohol; there was little or no loss in this operation.

After drying with calcium chloride, it was redistilled under ordinary pressure, using glass beads.

Weight of product taken = 248.0 g.

Fractions..... (1)a 71-120° (2)a 120-125° (3)a 125-128° (4)a 128-131°
34.6 g. 25.0 g. 32.7 g. 155.7 g.

Fractions (1)a, (2)a, and (3)a were then redistilled with the following results:

Refractionation of (1)a: B. p. 71-120°. Wt., 34.6 g.

(1)b below 120° (2)b 120-127° (3)b 127-130°
18.0 g. 2.6 g. 14.0 g.

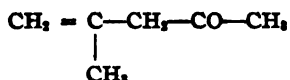
Refractionation of (2)a: B. p. 120-125°. Wt., 25.0 g.

(1)b below 120° (2)b 120-125° (3)b 125-131°
3.4 g. 3.2 g. 18.4 g.

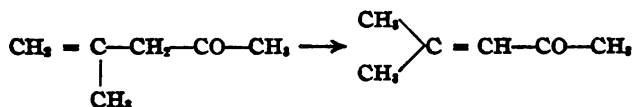
Refractionation of (3)a: B. p. 125-128°. Wt., 32.7 g.

(1)b below 120° (2)b 120-125° (3)b 125-128° (4)b 128-131°
1.1 g. 0.9 g. 6.0 g. 24.7 g.

It will be noted that in each case the boiling point of the distillate has risen appreciably, approaching more closely to that of mesityl oxide. This would seem to point to the probable presence of the second isomer:



which on distillation goes over into mesityl oxide:



That a mixture of acetone and mesityl oxide behaves quite normally on distillation under ordinary pressure is indicated by the following experiment:

13 g. acetone with 13 g. pure mesityl oxide were distilled together under ordinary pressure, using a fractionating column.

Fractions..... (1) B. p. 58-73° (2) B. p. 73-127° (3) 127-130°
10.5 g. 3.2 g. 12.0 g.

This shows that the presence of the acetone exercises little or no effect in lowering the boiling point of the mesityl oxide, and further that no mixture of constant boiling point exists.

Group III.—Synthesis of Unsaturated Aldehydes from Aldols.

Preparation of Crotonaldehyde from Acetaldol and Paracetaldol.—

The various processes described in the literature for the preparation of crotonaldehyde by direct distillation of acetaldol¹ give relatively poor yields (averaging about 50%, calculated on the weight of aldol taken) and the same remark applies to those methods involving the use of dehydrating agents, for example, potassium bisulfate.

The addition of a small quantity of iodine to the aldol, prior to the distillation, increases the yield of crotonaldehyde in a remarkable manner, as is shown in the following experiments:

Expt. I.—50 g. pure *paracetaldol* were distilled slowly from a small flask in the course of one hour, using a short fractionating column filled with glass beads. At the commencement of the distillation the thermometer in the neck of the column at once rose to 95°, remaining near this temperature almost throughout the experiment. An attempt to increase the rate of distillation caused the thermometer to rise at once to 140°, indicating only a partial decomposition into crotonaldehyde and water. The residue in the flask weighed about 7 g. The distillate, after separating off the water, was dried with CaCl₂, a further small quantity of crotonaldehyde being recovered by saturating the aqueous solution with the same reagent. The crude product weighed 27 g. On redistillation there were obtained:

Fractions. . . . I. 60–97°	II. 97–104° (principally 100–104°)	III. (above 104°)
2 g.	22 g.	2 g.

This represents a yield of some 55% crotonaldehyde, a considerable portion of the *paracetaldol* being decomposed into acetaldehyde.

Expt. II.—150 g. *acetaldol* were distilled under the same conditions as described in Expt. I. It was found that the product could be distilled rapidly without the thermometer going above 95°. A considerable quantity of liquid distilled over between 65–95°. After drying with CaCl₂ for 2–3 hours the crude product weighed 92.5 g. On refractionation there were obtained:

Fractions. . . . I. 40–70°	II. 70–96°	III. 96–104°	IV: Residue
13.0 g.	25.5 g.	47.0 g.	3.0 g.

No attempt was made to collect the product coming over below 40°. Fractions I, II, and III were again dried with CaCl₂ (I and II showed evidence of the presence of moisture, III was apparently quite dry) and redistilled.

Fraction I was found to consist principally of acetaldehyde.

Fraction II yielded four fractions:

¹ Orndorff and Newbury, *Monatsh. Chem.*, 13, 516 (1892); Grignard and Reif, *Bull. soc. chim.*, [4] 1, 114 (1907); McLeod, *Am. Chem. J.*, 37, 30 (1907).

(a) below 70° (principally 21–40°) (b) 70–97° (c) 97–104° (d) above 104°
6.0 g. 6.0 g. 10.5 g. 3 g.

Total amount of crotonaldehyde obtained was $47.0 + 10.5 = 57.5$ g., equivalent to a yield of 49%.

Effect of the Addition of a Small Quantity of Iodine.—Expt. III.—80 g. of pure *paracetaldol* were mixed with 0.08 g. iodine and distilled under the conditions described above, the entire operation occupying some 30 minutes. The thermometer in the column never indicated above 95°, and the residue left did not amount to more than about 7 g. After drying the distillate with CaCl_2 for 2–3 hours it was redistilled and found to boil very constantly at 100–104°. The distillate amounted to 52 g., equivalent to a yield of 82%, which, considering the mechanical losses, must be regarded as highly satisfactory. It was apparently a very pure product.

Expt. IV.—A similar experiment was carried out by distilling 200 g. *acetal*dol with 0.1 g. iodine over the naked flame. The operation took about two hours, the residue left in the flask amounting to 15 g. After drying with CaCl_2 , the crude product (wt. = 134 g.) was redistilled.

Fractions.....	I. 65–96°	II. 96–105°
	14.0 g.	114.5 g.

Fraction I was again dried and redistilled and then yielded 10 g. crotonaldehyde, b. p. 96–104°. The total weight of crotonaldehyde, b. p. 96–104° (principally 102–104°) obtained amounted to 124.5 g., corresponding to a yield of 80%.

In the course of these experiments several interesting facts relative to the behavior of crotonaldehyde came to light. It was found that a small quantity of water has the effect of lowering the boiling point of this substance appreciably, as shown in the following experiment:

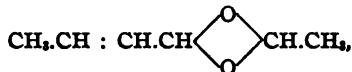
To 100 g. of pure crotonaldehyde (b. p. 102–104°) was added 0.5 g. water and the mixture distilled, using a fractionating column and beads:

Fractions.....	I. below 98°	II. 98–102°	III. 102–104°
	2.5 g.	30.5 g.	67 g.

Another point which calls for attention is the fact that whereas with *acetal*dol a lower boiling fraction (b. p. 65–96°) was always obtained along with the crotonaldehyde, this was not the case with *paracetaldol*. This lower boiling fraction, after very careful drying to remove all the water present, invariably decomposed on distillation, yielding a further quantity of acetaldehyde and crotonaldehyde, so that after several fractionations it was decomposed completely into these two products. The same phenomenon occurred when a large quantity (several hundred grams) of *well-dried* crotonaldehyde, b. p. 98–102° (that is, 2–4° below the true boiling point) was submitted to a careful refractionation. This gave a large amount of product boiling at a somewhat higher temperature, *viz.*, 102–104°, and a considerable quantity, b. p. 98–102°. This latter on being

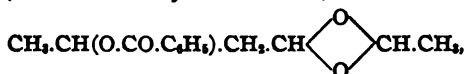
submitted to fractionation for a third time yielded some acetaldehyde, the product commencing to distil over below 30° , while a considerable quantity (about 17%) was collected between $85-98^{\circ}$. This latter also on re-fractionation gave a further quantity of pure crotonaldehyde, b. p. $102-104^{\circ}$.

It is an interesting speculation as to whether we are not dealing here with a compound of crotonaldehyde with acetaldehyde of the type



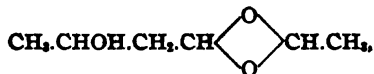
which decomposes into crotonaldehyde and acetaldehyde on repeated distillation. The fact that acetaldol gives rise to this lower-boiling mixture, while paracetaldol does not, is perhaps to be connected with the relatively greater ease of dissociation of the former back again into acetaldehyde.

The above body would be analogous to the one formed from acetaldol and acetaldehyde, whose benzoyl derivative,

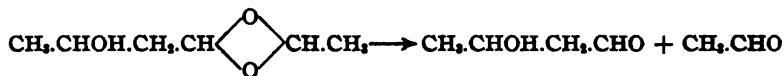


was obtained by P. C. Freer¹ by the action of sodium on acetaldehyde and benzoyl chloride in ether solution.

There would also seem to be an indication of the actual existence of the parent substance,



in the fact that the distillation of the crude product obtained by the condensation of acetaldehyde to acetaldol by various alkaline reagents, under widely varying conditions, almost invariably gives a yield of approximately 66% aldol, and 33% acetaldehyde, thus pointing to the probable existence of this in the condensation product, and to its decomposition



on heating.

These experiments will be described in a later communication.

Group IV.—Synthesis of Polyglycols and Polyglycerols.

(a) **Preparation of Polyglycol from Butylene Glycol.**—200 g. of butylene glycol were mixed with 1.0 g. iodine and heated in a distilling flask, using a fractionating column, for about 8 hours in an oil-bath, the temperature of the latter being so regulated that the thermometer in the distilling flask never showed a temperature higher than about 130° . About 80

¹ *Ann.*, 293, 326 (1896).

g. distilled over, consisting apparently of crotyl alcohol, water and some other by-products. The residue in the flask was then distilled under reduced pressure, and after about 20–30 g. of butylene glycol had passed over at 175°, under a pressure of 20–25 mm., the temperature rose rapidly to about 200°, the remainder (about 80 g.) distilling over between 200–350°, under the above pressure. The product was not examined further, but consisted presumably of polyglycols.

(b) **Syntheses of Polyglycerols.**—The following examples are typical of a number carried out under somewhat similar conditions:

Experiment I.—1518 g. C. P. anhydrous glycerol were mixed with 1/3000 of its weight (0.506 g.) iodine and the product heated in an oil bath at ordinary pressure for 7 hours, the flask being connected with a condenser. A slow stream of carbon dioxide was passed through the apparatus throughout the experiment, the temperature of the oil bath being maintained at 210–215°. During this period 120 g. of distillate were obtained, principally water with some glycerol.

The remaining product was then distilled under reduced pressure with the following result:

Fraction (1) Aqueous distillate passing over at ordinary pressure.....	= 120.0 g.
Fraction (2) Water + glycerol (below 184° at 23 mm.).....	= 82.0 g.
Fraction (3) Glycerol, b. p. 169° at 5 mm.....	= 592.0 g.
Fraction (4) Glycerol and polyglycerol, b. p. 169–183° at 4 mm.....	= 265.0 g.
Fraction (5) Glycerol and polyglycerol, b. p. 183–226° at 4 mm.....	= 113.0 g.
Fraction (6) Polyglycerol, b. p. over 226° at 4 mm.....	= 346.0 g.
	<hr/>
	1518.0 g.

On account of the difficulty in separating polyglycerol from glycerol, no accurate estimate of the yield can be made, but assuming that Fractions 5 and 6 represent a diglyceride, this would represent some 33% by weight of that of the glycerol originally taken. In an attempt to isolate a constant-boiling product, Fraction 6 was redistilled under reduced pressure. The temperature rose rapidly to 235° at 5 mm. and 195 g. distilled over between 235–284° with the pressure gradually rising from 5 to 31 mm. A third refractionation of the 195 g. thus obtained gave

Fraction (1)	27.0 g. below 234° at 5 mm.
Fraction (2)	122.0 g. 234–240° at 3–5 mm. (principally 234–236 at 3 mm.)
Fraction (3)	46.0 g. above 240° at 3 mm.

Experiment II.—814 g. of C. P. anhydrous glycerol were mixed with 1/3000 of its weight (0.271 g.) iodine and heated for 1 hour at ordinary pressure under the same conditions as described in Expt. I, the temperature of the oil bath being 210–215°. It was then heated for one hour under reduced pressure (45–55 mm.) at the same temperature, after which the product was distilled under reduced pressure.

Fraction (1) Water and glycerol.....	= 78.0 g.
Fraction (2) Glycerol, b. p. 169° at 5 mm.....	= 450.0 g.
Fraction (3) Glycerol and polyglycerol, b. p. 170–220° at 3 mm.....	= 145.0 g.
Fraction (4) Polyglycerol, b. p. 220–237° (principally 225–235° at 3 mm.)	= 87.0 g.
Fraction (5) Residue.....	= 54.0 g.
	<hr/>
	814.0 g.

The somewhat lower boiling point of the polyglycerol obtained in Fraction 4 in comparison with Expt. I is probably due to the fact that in Experiment I a metal, and in Expt. II an oil bath was used for heating the flask during the distillation.

Experiment III.—457 g. C. P. anhydrous glycerol were mixed with 1/5000 of its weight (0.091 g.) of iodine and heated for 7 hours at ordinary pressure under same conditions as in Expt. I. At the end of this period the product was distilled under reduced pressure.

Fraction (1) Water and glycerol.....	= 27 g.
Fraction (2) Glycerol, b. p. below 175° at 3 mm.....	= 312 g.
Fraction (3) Residue in flask.....	= 109 g.

Apparently reducing the amount of iodine from 1/3000 to 1/5000 diminishes the yield appreciably, under the same conditions.

Experiment IV (Blank Experiment).—314 g. of C. P. anhydrous glycerol were heated for 5 hours at ordinary pressure under same condition as in Expt. III. Only a few drops of water passed over and on distilling the product under reduced pressure it boiled constantly at about 170° at 8–10 mm. Not more than 5 g. of high-boiling product remained behind.

The experiment is of interest in bringing out more clearly the action of the iodine in facilitating the condensation.

Group V.—Condensation of Glycols with Aldehydes.

Preparation of 1-Methyl Propane-diol-ethylal.—Fifty grams of butylene glycol were mixed with 60 g. acetaldehyde, and 0.3 g. iodine added. The mixture was heated on the water bath, using a reflux condenser, for about 4–6 hours. The excess of acetaldehyde was then distilled off, using glass beads, and the fraction passing over between 40–180° redistilled after drying with potassium carbonate. 55.5 g. of a product, b. p. 110–125° (principally 118–120°) were obtained. This represents a yield of 86% of 1-methyl propane-diol-ethylal obtained by the condensation of one molecule of butylene glycol, with one molecule of acetaldehyde.

Presumably the quantity of iodine employed could be materially diminished, as well as the time of heating, and the yield could probably be increased.

The condensation is also brought about by the use of a small amount of 20% sulfuric acid.

Summary.

A description has been given of various experiments carried out illustrative of the use of iodine as a dehydrating and condensing agent. In all the cases investigated, *viz.*:

- (a) Conversion of alcohols into unsaturated hydrocarbons.
- (b) Conversion of ketone-alcohols into unsaturated ketones.
- (c) Conversion of aldols into unsaturated aldehydes.
- (d) Conversion of glycols and glycerols into polyglycols and polyglycerols, respectively.
- (e) Condensation of aldehydes with polyalcohols.

It has been found that a very small amount of iodine (in some cases as low as 1/10,000 part by weight) suffices to bring about the change. The reaction is apparently a general one, and a tentative theory has been advanced to explain the catalytic role played by the iodine in such processes.

In two recent patents¹ the claim is made that the presence of small traces of iodine induces in a remarkable manner the condensation of amines with alcohols (*e. g.*, formation of dimethylaniline from aniline and methyl alcohol) as well as the splitting off of HCl from amines and their hydrochlorides, so that it would not be at all surprising if this reagent should prove capable of an extremely wide application in synthetic organic work both in the laboratory and in the industry.

The greater part of the preceding investigation was carried out at the Experimental Station of the E. I. duPont de Nemours Powder Co., Wilmington, Del., and the author wishes to express his thanks to the officials of this company for the facilities placed in his way in enabling him to carry out the work.

PITTSBURGH, PA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORIES.]

THE ACETOLYSIS OF CARBOHYDRATES.

By S. BORN AND J. M. NELSON.

Received May 22, 1915.

The study of the acetolysis of the carbohydrate part of invertase² led to the following work on the acetolysis of other carbohydrates. It was hoped that by an extensive study of a large number of these disaccharides and polysaccharides, we might be able to formulate some general principle regarding the structure of these compounds from their behavior on acetolysis, and thus throw more light on the constitution of the carbohydrate part of invertase.

It has been noticed in the acetolysis of various disaccharides and poly-

¹ Knoll and Co., D. R. P. 241,853, 250,326.

² THIS JOURNAL, 36, 398 (1914).

saccharides, that the breaking down of these sugars through the agency of acetyl chloride, acetyl bromide or acetyl sulfate (acetic anhydride + concentrated sulfuric acid), comes to an end at the monosaccharide stage in certain cases, while in others it stops at the disaccharide stage. The question whether this difference in behavior can be attributed to the nature of the oxygen linking connecting the monosaccharides, or to the character of the monosaccharides themselves, has led us to undertake the present investigation.

Syniewski,¹ from an exhaustive study of the behavior of starch on hydrolysis, suggested that there are three different types of linkings between the various glucose molecules. These three are the α -linking, which is readily hydrolyzed by malt, yielding maltose and a dextrin; the β -linking, which is difficultly broken by malt yielding glucose and a dextrin; and the γ -linking which connects the glucose in maltose itself. The above hypothesis readily explains why we obtain various products in hydrolyzing starch, the nature of the product depending upon which linking is attacked by our hydrolyzing agent.

When we treat polysaccharides, disaccharides and glucosides with acetolytic agents, we notice a similar behavior. That this difference in behavior depends on the nature of the linking and not on the character of the monosaccharides constituting the sugars, may be seen most readily in the case of those polysaccharides where the monosaccharides are all the same, like cellulose and starch.

Hardt and Strehmayer,² and more recently Klein,³ studied the acetolysis of cellulose with acetic anhydride and sulfuric acid. They obtained products ranging from cellulose acetates down to cellobiose acetates, but in no case could they obtain glucose acetates, although Klein looked for them, showing that there must be a different linking between the glucose molecules composing cellobiose, and those linking it to the rest of the molecule.

Skraup⁴ and Klein both noted that the amount of sulfuric acid and temperature influenced the speed of reaction, and not the final products. In no case could cellobiose acetate be broken down further.

Pregl⁵ investigated the acetolysis of soluble starch with acetic anhydride and sulfuric acid, and isolated several dextrin acetates. His work does not, however, indicate what happens to these on further acetolysis.

The action of the three acetolytic agents on the various disaccharides which have been studied is indicated briefly in Table I.

¹ *Ann.*, 324, 212 (1901).

² *Monatsh.*, 28, 63 (1907).

³ *Z. angew. Chem.*, 25, 1409 (1912).

⁴ *Ber.*, 32, 2413 (1899).

⁵ *Monatsh.*, 22, 1049 (1901).

TABLE I.

	Acetic anhydride + sulfuric acid.	Acetyl chloride.	Acetyl bromide.
Cellulose	Cellobiose octacetate (Hardt and Strehmayer) ¹	Acetchlorocellobiose (Bates) ⁷	Acetbromocellobiose (Bates) ⁷
Starch	Dextrin acetates (Pregl) ²		
Maltose	Maltose octacetate (Born and Nelson) ³	Acetchloromaltose (Born and Nelson) ⁴	Acetbromomaltose (Fischer) ⁵
Lactose	Lactose octacetate (Bodart) ⁴	Acetchlorolactose (Born and Nelson) ⁶	Acetbromolactose (Ditmar) ⁶
Sucrose	α -Glucose pentacetate (Skraup) ⁶	Acetchloroglucose (Born and Nelson) ⁶	Acetbromoglucose (Born and Nelson) ⁶
α -Methyl glucoside	α -Pentacetyl glucose (Born and Nelson) ⁶		

As can be noticed from the table, the knowledge up to the time we started our work was not in such condition that any comparison could be made as to the acetolytic action of these reagents on the various carbohydrates. By filling in the gaps in the table this has been made possible. The experimental work follows.

Experimental.

I. Action of Acetyl Bromide on Sucrose.—Five grams of sucrose, dried at 50° in a vacuum over phosphorus pentoxide, were treated with 25 g. of acetyl bromide, and heated gently on a water bath until all had gone into solution. The pale yellow syrup was dissolved in ether, washed with sodium sulfite and sodium carbonate, dried over calcium chloride, and then evaporated *in vacuo* at room temperature to a thick syrup. This syrup was dissolved in hot ligroin, b. p. 70–80°. On cooling, needle-shaped rosetts, easily soluble in xylene, separated, m. p. 88–9° (uncor.). Reduces Fehling's solution. Identified as acetbromoglucose.

On analysis: Found, Br = 19.55%. Calc., Br = 19.46%.

II. Action of Acetyl Chloride on Sucrose.—Five grams of dried sucrose were treated with 15 g. of acetyl chloride and allowed to stand at room temperature for three days, when most had gone into solution. The light yellow solution was treated in the same way as the product from the action of acetyl bromide, but all attempts to obtain crystals from it have failed.

¹ *Monatsh.*, 28, 63 (1907).

² *Ibid.*, 22, 1049 (1901).

³ *Ber.*, 34, 2895 (1902); 35, 840 (1903).

⁴ *Chem. Ztg.*, 25, 1039 (1901); *Monatsh.*, 23, 1 (1902).

⁵ *Ber.*, 35, 1953 (1902); *Monatsh.*, 23, 865 (1902).

⁶ *Ber.*, 32, 2413 (1900).

⁷ Private communication. J. S. Bates, working in this laboratory, has prepared the above compounds by the action of acetyl chloride and bromide on cellulose. The details will be published shortly.

⁸ These gaps in the table have been filled in by our work.

The syrup gave strong tests for halogen and reduced Fehling's solution, showing that it was probably acetochloroglucose, which is very difficultly crystallizable.

III. Action of Acetyl Bromide on Maltose.—Five grams maltose dried at 100° in vacuum over phosphorus pentoxide were treated with 20 g. of acetyl bromide. Reaction started immediately and all went into solution in a short while. The solution was dissolved in ether, washed with ice-cold solution of sodium sulfite and carbonate, the ethereal solution dried over calcium chloride, and evaporated *in vacuo* at room temperature. A white, amorphous powder was obtained, soluble in benzene, acetone, alcohol, slightly in ligroin and petroleum ether. All attempts to crystallize it failed. Our substance agreed in every respect with that obtained by Fischer,¹ who used the same method. The substance is acetbromomaltose.

Analysis: Found, Br = 11.24%. Calc., Br = 11.44%.

IV. Action of Acetyl Chloride on Maltose.—Five grams of maltose dried at 100° *in vacuo* over phosphorus pentoxide were treated with 25 g. acetyl chloride. Over night most had gone into solution. The solution was dissolved in ether, washed with sodium sulphite and sodium carbonate, dried over calcium chloride, evaporated *in vacuo* to a glistening, white powder. All attempts to crystallize this substance failed. Attempts were made to purify it by dissolving it in benzene, and precipitation with ligroin. The crude substance melted at about 65°, not sharply, is soluble in ether, benzene, toluene, xylene, alcohol, reduces Fehling's solution. Analysis showed Cl content about that of acetchloromaltose.

Analysis: Found, Cl = 4.35%. Calc., Cl = 5.42%.

V. Action of Acetic Anhydride and Sulfuric Acid on Maltose.—Five grams of maltose dried at 100° *in vacuo* over phosphorus pentoxide were treated with a mixture of 25 cc. acetic anhydride and 0.25 cc. of sulfuric acid previously cooled. All went into solution without charring. The solution was poured into water. A gum precipitated, which was washed well with water, till free of acetic anhydride, dissolved in alcohol, and reprecipitated with water. A white, amorphous powder, which we were unable to crystallize, separated out. The substance is octacetylmaltose.

Acetyl values: 49.6, 49.0; calc., 50.7%.

VI. Action of Acetyl Chloride on Lactose.—Five grams of lactose dried in vacuum at 110° over phosphorus pentoxide were treated with 20 cc. acetyl chloride. After all had gone into solution, the syrup was dissolved in chloroform diluted with ether, washed with ice-cold sodium sulfite and sodium bicarbonate, the ethereal solution dried over calcium chloride, and evaporated *in vacuo* at room temperature. A glistening, white pow-

¹ Ber., 42, 2523 (1910).

der, which could not be crystallized, was obtained. It is soluble in benzene, xylene, alcohol, slightly soluble in petroleum ether and ligroin.

VII. Action of Acetic Anhydride and Sulfuric Acid on α -Methyl Glucoside.—Two grams of α -methyl glucoside dried to constant weight at 100° were treated with a mixture of 10 cc. of acetic anhydride and 0.5 cc. sulfuric acid. All went into solution in a short while. The solution was poured into water and the precipitate recrystallized from alcohol. White needles, m. p. $111-112^{\circ}$. It reduces Fehling's solution and was identified as α -pentacetyl glucose by the melting point, and mixing some with a known sample of α -pentacetyl glucose. The melting point of the mixture was the same.

VIII. Action of Acetyl Bromide on α -Methyl Glucoside.—Five grams of dried α -methyl glucoside were treated with 20 g. of acetyl bromide. The reaction started at ordinary temperature with brisk evolution of hydrobromic acid. When all had gone into solution, it was dissolved in ether, washed with sodium sulfite and sodium bicarbonate, the ethereal solution dried over calcium chloride, evaporated *in vacuo*. A light brown syrup, soluble in benzene, alcohol, insoluble in ligroin, and which could not be crystallized was obtained.

IX. Action of Acetyl Bromide on Inulin.—Inulin was purified by dissolving a good grade of inulin in hot water, filtering from insoluble matter, and precipitating with three times its volume of alcohol. This was repeated three times when the inulin no longer reduced Fehling's solution. The inulin was first dried over sulfuric acid in a vacuum desiccator and then for five hours at 100° over phosphorus pentoxide *in vacuo*.

Five grams of inulin thus purified were placed in a flask, packed with ice, and 25 cc. of acetyl bromide, also cooled, added. The mixture was allowed to stand in ice about twelve hours, when all had gone into solution. Great care must be used in keeping down the temperature to avoid charring. The yellow syrup obtained above was dissolved in ether, washed with ice-cold sodium sulfite and sodium carbonate solution; the ethereal solution was dried over calcium chloride, filtered, and the ether was evaporated *in vacuo* at low temperature. A yellow syrup remained which resisted all attempts to crystallize it. The syrup reduced Fehling's solution. Several bromine determinations were made on this syrup, but as the product is very impure they did not check.

An average analysis is:

0.8685 g. subs. gave 0.2610 g. AgBr = 12.7% Br. Calc. for acetbromofructose = 19.46% Br; for acetbromodisaccharide = 11.44% Br.

Five grams of crude acetate prepared above were shaken with an excess of barium hydroxide solution until nearly all had gone into solution. The solution was filtered, the filtrate saturated with carbon dioxide, the barium carbonate filtered off, and the filtrate evaporated *in vacuo*

to syrup. The syrup is soluble in alcohol, reduces Fehling's solution, and gives an osazone which was identified as fructosazone (glucosazone). The substance resisted all attempts to crystallize it.

Summary.

1. Sucrose treated with acetyl bromide gives acetbromoglucose.
2. Sucrose treated with acetyl chloride gives acetchloroglucose.
3. Maltose treated with acetyl bromide gives acetbromomaltose.
4. Maltose treated with acetyl chloride gives acetchloromaltose.
5. Maltose treated with acetic anhydride and sulfuric acid gives oct-acetyl maltose.
6. Lactose treated with acetyl chloride probably gives acetchlorolactose.
7. α -Methyl glucoside treated with acetic anhydride and sulfuric acid gives α -pentacetyl glucose.
8. α -Methyl glucoside treated with acetyl bromide gives an unidentified syrup.
9. Inulin treated with acetyl bromide gives an unidentified syrup.
10. From the work so far we feel justified in concluding that there is a marked difference in stability toward acetolysis by different oxygen linkings in disaccharides and polysaccharides.
11. Acetyl chloride, bromide, and sulfate show similar acetolytic action.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

SOME CONSTITUENTS OF THE ROOT OF *BRAUNERIA* *ANGUSTIFOLIA*.

BY FREDERICK W. HEYL AND MERRILL C. HART.

Received April 30, 1915.

In a report of the Council on Pharmacy and Chemistry¹ of the American Medical Association, the root of *Brauneria angustifolia*, commonly

¹ *J. Am. Med. Assoc.*, 53, 1836 (1909).

known as *Echinacea* is stated to be without therapeutic value. Nevertheless, there is a sufficient demand for the root to make it profitable for a number of agriculturists, especially in Kansas and Nebraska, to supply the present requirements of the pharmaceutical market. This demand for the drug consists, not only for use in the several patent medicines enumerated in the above mentioned report, but also for nonofficial unadvertised preparations, such as the common fluid extract.

For this reason it has been considered of interest to subject the root to a chemical study, to learn if the chemical evidence gained would be of any value in forming a more definite conclusion upon its therapeutic properties. No physiologically active substance was isolated, and the results herein reported may, therefore, be considered as partially confirmatory to the report of the Council.

The study of the plant was made as nearly quantitative as possible and we have endeavored to state the weights of the many fractions into which the alcohol soluble constituents were separated. A review of the quantities of the indefinite noncrystalline substances, as compared with the weights of the plant constituents which could be identified, indicates that the former products very greatly preponderate. In view of these facts the chemical evidence cannot be considered conclusive.

In an earlier paper¹ from this laboratory the proximate analysis of this root was reported. It was shown that the air-dried root contained 10.9% moisture and 7.8% ash. Ligroin extracted 0.77%; ether, 1.2% and alcohol 19.7% (of which only 0.14% is inorganic). The residue insoluble in alcohol had the following composition: crude fiber, 24.7%; pentosans, 15.6%; protein, 6.9%; inulin, 5.9%. An "inuloid" product amounting to about 6.0% was also present. These results account for about 98% of the plant. The presence of inulin and inuloids rather than starch and dextrins causes this summation to be subject to some error, because of the lack of well-known methods for the determination of inulins.

The alcoholic extract showed the presence of about 7.0% sucrose and 4.0% 1 vulose. The resin amounts to 1.9% of the air-dried plant. Of the 19.7% dissolved by alcohol these substances amount to 12.9%, leaving 6.8% unaccounted for.

We report the examination of the products present in the alcoholic solution and soluble in water, and of the ligroin, ether, chloroform, ethyl acetate, and alcoholic extracts of the resin which was insoluble in water.

The aqueous solution yielded traces of a phenolic acid agreeing in composition with the formula $C_9H_{10}O_6$ and melting at 207° ; an amorphous glucosidic amyl alcohol extract amounting to 0.3%; betaine, 0.1%; and the sugars above mentioned.

The ligroin extract of the resin yielded oleic, linolic, cerotic and palmitic

¹ *Am. J. Pharm.*, 86, 451 (1914).

acids; two isomeric phytosterols, $C_{27}H_{46}O$, one melting at $154.5-156.5^{\circ}$ and forming an acetate melting at $131.5-132^{\circ}$, while the other phytosterol melted at $136-137^{\circ}$ and formed an acetate melting at $118-120^{\circ}$. The ether extract yielded a phytosterolin melting at $280-290^{\circ}$ and agreeing in composition with the formula $C_{32}H_{50}O_6$. The acetate of this compound melted at $163-164^{\circ}$.

The chloroform, ethyl acetate, and alcoholic extracts of the resin yielded no definite products.

Experimental.

The material used in this investigation, amounting to 33.3 kg. of the air-dried drug, was exhausted by percolation with 95% alcohol. The percolate, which amounted to 260 liters, was concentrated under diminished pressure to a volume of 11.5 liters. The resin was completely precipitated by mixing this alcoholic solution with about 20 liters of distilled water. By siphoning, most of the aqueous layer was readily separated from the supernatant resin. We thus obtained two fractions, (1) the plant substances soluble in water, (2) the resin, a brownish yellow product, which failed to give any evidence of crystallization from solution in 95% alcohol at various concentrations.

Examination of the Aqueous Solution.—This clear reddish brown solution was concentrated under diminished pressure to a volume of about ten liters and extracted repeatedly with large volumes of ether. The ethereal solution, which contained not more than 5 g. of material, was concentrated to a small volume and fractionally extracted with solutions of hydrochloric acid (10%) water, ammonium carbonate, sodium carbonate, and potassium hydroxide successively. The last two solvents extracted nothing which could be identified.

The hydrochloric acid extracts of the ether extract were dark brown in color, and upon standing gave smeary precipitates. Tests with Mayer's reagent and with iodine in potassium iodide solution gave slight but positive results in the first five acid extracts.

Each of the ammonium carbonate extracts was acidified separately. The first extract gave an oil which, after standing several days, showed the presence of a small quantity of a crystalline body. The subsequent extracts gave similar results, but with the presence of smaller amounts of the smeary material. The acid liquid was in each fraction poured off from this precipitate and the residue, after drying in a vacuum over sulfuric acid, was allowed to stand with a small volume of anhydrous ether, which readily dissolved the smear and left a residue of the crystalline material. These products amounted to less than 0.1 g. As the product was obviously impure and insufficient to work with, the original aqueous extract was concentrated sharply to a volume of 5.5 liters and

again extracted with ether. The ether extracts were worked up as before, but the additional quantity of substance isolated was very slight.

The material separating upon acidification of the ammonium carbonate extracts, was united in one fraction and dissolved in absolute methyl alcohol. It was then esterified with dry hydrochloric acid gas in the usual manner. The solvent was removed and the esters dissolved in ether. The ethereal solution was extracted with water and with ammonium carbonate. Most of the product was extracted with dilute potassium hydroxide solution, thus indicating the presence of a phenolic ester. The alkaline extract was concentrated to a small bulk on the water bath in order to saponify the ester. Upon acidification an acid separated in colorless needles, which, after recrystallization from water, melted at about 207° . Upon elevating the temperature in the capillary tube above the melting point the evolution of a gas ensued. This product gave no color test with a solution of ferric chloride and upon analysis gave results which agree with an acid having the formula $C_9H_{10}O_6$, possibly a trioxyphenylpropionic acid.

0.0564 g. subst. gave 0.1125 g. CO_2 and 0.0262 g. H_2O . Calc. for $C_9H_{10}O_6$: C, 54.5; H, 5.1; found: C, 54.4; H, 5.2.

The aqueous solution which had been completely extracted with ether was now extracted repeatedly with hot amyl alcohol. By carefully concentrating the various amyl alcohol extracts there was obtained several crops of brown, amorphous material which, being similar in appearance, were joined. This product could not be crystallized. An acid hydrolysis yielded nothing crystalline. It yielded, however, a quantity of *d*-phenylglucosazone melting at $202-203^{\circ}$.

The filtrates from which the above mentioned brown amorphous product had separated were studied separately but could not be brought to crystallization. When the amyl alcoholic solution was precipitated with ligroin, the material separated as a smear. By precipitation with ether it was found possible to prepare a light, amorphous product from the latter fractions, whereas the products from the first three of the amyl alcoholic extracts were of a syrupy consistency.

All of this material was brought into one fraction. The weight was approximately 95 g. The amyl alcohol fraction therefore amounts to about 0.31% of the root.

Forty-two grams of this material were boiled for one minute with 10% aqueous potassium hydroxide in the presence of sufficient alcohol to retain it in solution. Nothing of interest was isolated; another portion, amounting to 50 g. and entirely free from material reducing Fehling's solution, was boiled with 21 g. of sulfuric acid for $2\frac{1}{2}$ hours in the presence of 500 cc. dilute alcohol. On standing over night a heavy smear separated. The supernatant liquid was poured from the resin and dis-

tilled in a current of steam. Although this acid hydrolysis was accompanied by the evolution of a product having an odor similar to furfuraldehyde, the steam distillate failed to give a positive test for this. The steam distillate contained, floating upon the surface, an appreciable quantity of an oil which was not identified.

The acid liquid which had been distilled with steam was extracted with ether. The ether yielded traces of an acid melting at $203-205^{\circ}$ and identical with the one previously described.

The aqueous liquid which had been extracted with ether showed, when quantitatively studied as regards its reducing action upon Fehling's solution, the presence of a sugar amounting to 3.2 g. calculated as dextrose. It yielded *d*-phenylglucosazone melting at $203-204^{\circ}$.

The products extracted with amyl alcohol are, therefore, shown to be partially glucosidic in their nature. They possess, in part at least, the bitter taste of *Echinacea* root.

The aqueous liquid which had been extracted with ether, and with amyl alcohol, was freed from the latter immiscible solvent by means of a vigorous steam distillation. The total volume at this point was 8.8 liters.

100 cc. gave, with lead subacetate, a precipitate containing 0.0871 g. nitrogen.

100 cc. gave, when distilled with MgO, 0.0129 g. nitrogen as ammonia.

25 cc. gave a quantity of nitrogen equivalent to 0.5004 g. per 100 cc. by the Kjeldahl method.

The distribution of nitrogen is therefore as follows: Total soluble nitrogen = 0.132%; ammonia nitrogen = 0.0034%; lead subacetate precipitable nitrogen = 0.023%; nitrogen precipitated with phosphotungstic acid = 0.032%.

Obviously, a large part of the nitrogenous constituents is not accounted for in the above table. In order to test for acid amides such as asparagine and glutamine, one-fifth of the solution was precipitated with mercuric acetate solution, but only a very slight separation took place. Its subsequent examinations for asparagine, glutamine and allantoin were negative.

The remaining four-fifths was completely precipitated with basic lead acetate, whereupon a heavy precipitate separated. This was removed by filtration and decomposed with hydrogen sulfide in the usual manner. This dark-colored solution gave, with ferric chloride solution, a very slight greenish color. The usual tests for tannin were negative. An effort to prepare copper salts from the solution proved futile and an alkaline hydrolysis yielded no definite products. This fraction contained about 168 g. of amorphous material.

The filtrate from the above precipitation was freed from the excess of lead with hydrogen sulfide and after filtering off the lead sulfide, the filtrate was concentrated to a syrup, which contained 2967 g. of material (dried at 100°). A quantity (535 g.) was precipitated with an excess (180 g.) of phosphotungstic acid in the presence of 5% sulfuric acid. A heavy precipitate resulted. This was removed by filtration, washed

with 5% phosphotungstic acid wash and decomposed by the method of Wechsler.¹ The solution of the basic products was made up to a volume of 2000 cc.

25 cc. distilled with MgO yielded no ammonia.

100 cc. required by Kjeldahl method 54.5 cc. 0.1 N acid.

Of the 2000 cc. solution, 600 cc. were concentrated to a syrup at 33°. To this was added 350 cc. of absolute alcohol. A separation of 0.72 g. of amorphous material took place. The filtrate from this material was concentrated to a syrup which weighed about 6 g., and it was now readily soluble in absolute alcohol. To this alcoholic solution an excess of concentrated hydrochloric acid was added, and after standing a short time beautiful crystals of betaine hydrochloride formed. Altogether, 1.45 g. of betaine hydrochloride, equivalent to 0.08% of the plant were obtained. The melting point was 237–238°.

Calc. for $C_5H_{11}O_2N.HCl$: Cl, 23.1%; found: Cl, 22.85%.

It formed the double platinum salt, which melted at 242°.

Calc. for $(C_5H_{11}O_2N.HCl)_2PtCl_4$: Pt, 30.3%; found: Pt, 30.8%.

It is evident that the betaine isolated quantitatively as the hydrochloride fails to account for the total nitrogen in this fraction, for the quantity of nitrogen due to betaine is only 0.44 g., against 1.53 g. known to be present in the 2000 cc. solution. This nitrogenous product is present in the filtrate of the betaine hydrochloride but was not identified.

The study of these nitrogenous constituents was repeated upon a larger quantity, following the comprehensive methods outlined by E. Schulze and E. Winterstein.² A slight separation of a purine fraction was obtained but nothing could be isolated from it. The arginine and histidine fraction was absent. The material was precipitated for the second time with phosphotungstic acid, and betaine hydrochloride quantitatively separated as before. The alcoholic, neutral filtrate was precipitated with a saturated alcoholic solution of mercuric chloride, whereupon a thick, black oil separated, but no crystalline mercuric salts could be obtained. The oil, as well as the filtrate from it were treated with hydrogen sulfide, but no crystalline products could be prepared.

The other products of the syrupy liquid, as has been shown in another paper,³ are levulose and sucrose. This syrup yielded a heavy crystalline deposit of *d*-phenylglucosazone melting with decomposition at 203–205°.

Examination of the Resin.—The resin weighed 628 g. It was extracted in the usual manner with various solvents with the following results: ligroin, 222 g.; ether, 107 g.; chloroform, 180 g.; ethylacetate, 35 g.; alcohol, 70.0 g.

¹ *Z. physiol. Chem.*, 73, 138 (1911).

² *Handbuch der Biochem. Arbeitsmethoden*, Vol. II, p. 518.

³ *Loc. cit.*

The Ligroin Extract.—For the further examination of this material 157 g. were dissolved in 500 cc. of ether. The ether solution was extracted with small portions of 5% and 10% hydrochloric acid solutions. These were made alkaline and extracted with chloroform. The chloroform solution gave a slight test for alkaloids with Mayer's reagent, but on evaporation of the solvent a small, oily residue was left from which nothing was obtained. The ethereal solution was then extracted successively with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. The potassium carbonate extract yielded, upon acidification, 40 g. of fatty acids. This was completely soluble in ligroin. The ligroin solution was dried over anhydrous sodium sulfate, filtered and the ligroin removed. The residue distilled under diminished pressure, boiled for the most part from 236–276° at 33 mm. The iodine numbers of the fractions varied from 75.8 to 82.8.

The fatty acids were then separated into their solid and liquid components by the usual method. From 23 g. of the mixed fatty acids, 12.9 g. of liquid acids were obtained, which were distilled under diminished pressure.

Fraction.	Pressure. Mm.	Temperature.	Iodine. numbers.
1.....	17–18	168–200°	...
2.....	17–18	210–240	119.7
3.....	17–18	240–273	116.2
4.....	17–18	273–294	100.6

A combustion was made on Fraction II.

Calc. for $C_{18}H_{34}O_2$: C, 76.59; H, 12.06; for $C_{18}H_{32}O_2$: C, 77.1; H, 11.4; found: C, 77.44; H, 11.64.

The iodine numbers, as well as the results of the combustion, indicate the liquid acids to be a mixture of *oleic* and *linolic* acids with oleic acid predominating.

The potassium hydroxide extractions of the ethereal solution gave only a slight amount of an oily residue, which was examined in conjunction with the fatty acids obtained after the hydrolysis of the glycerides with alcoholic potash.

After the ethereal solution had been extracted with potassium hydroxide the ether was removed and the residue saponified with alcoholic potash. The alcohol was removed and the residue diluted with water. This alkaline solution was then extracted many times with ether.

The aqueous solution of the potassium salts, after the removal of the unsaponifiable matter by means of ether, was acidified and then again extracted with ether. The ethereal solution was washed, dried and the ether removed. On dissolving the residue in a large volume of low boiling petroleum, a small quantity of resinous matter was precipitated. The petroleum was then removed and the residue distilled under diminished

pressure. The weight of distilled acids was 48.5 g. (iodine number = 101.9). These acids were separated into the solid and liquid components by the usual method. Nineteen grams of liquid acid and 24.6 g. of solid fatty acid were obtained. The liquid acids were then distilled again under diminished pressure. Most of the acid came over at about 200° at 11 mm.

Fraction.	Temperature.	Pressure, Mm.	Iodine number.
1.....	...-175°	11	...
2.....	175-215	11	141.4
3.....	215-230	11	147.7
4.....	230-250	11	118.4

To gain further insight into the nature of these acids they were oxidized by the method outlined by Lewkowitsch.¹

Dioxystearic acid, melting at 129.5-130.5° was isolated. Saticic acid was obtained upon the oxidation of the liquid acids occurring free in the fat; and also from the acids obtained after hydrolysis. The melting point was 155-158°. The melting point after a large number of crystallizations from alcohol was raised to 170.5-172°.

Calc. for $C_{18}H_{34}O_4$: C, 62.1; H, 10.3; found: C, 61.8; H, 10.5.

The Solid Fatty Acids.—The solid fatty acids amounting to 27.2 g. derived from the hydrolysis of the glycerides were united with those that occurred free in the fat and subjected to fractional crystallization from absolute alcohol. The first fraction that separated, when recrystallized from absolute alcohol, weighed 0.7 g. and melted at 77-78°. After one more crystallization from alcohol it melted at 77.5-78.5°. It was identified as cerotic acid.

Calc. for $C_{26}H_{52}O_2$: C, 78.8; H, 13.1; N. V., 141.7; found: C, 78.6; H, 13.1; N. V., 140.4.

Fraction II after several crystallizations from absolute alcohol melted at 53.5 to 55.5°.

Calc. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5; N. V., 219.1.

For $C_{18}H_{36}O_2$: C, 76.1; H, 12.7; N. V., 197.5.

Found: C, 75.26; H, 12.33; N. V., 202.8.

This is impure palmitic acid.

Fraction III, after several crystallizations from absolute alcohol, melted at 55-57°.

0.4842 g. neutralized 0.973 g. KOH. Neutralization value² = 200.4.

Examination of the Unsaponifiable Matter.—The ethereal solution was gradually concentrated but no hydrocarbons separated. Upon the complete removal of the ether a partially crystalline residue amounting

¹ "Chemical Technology and Analysis of Oils, Fats and Waxes," p. 564.

² Lewkowitsch, Vol. 1, p. 518. Tortelli and Pergami obtained a value of 202.7 for palmitic acid when titrated in the cold. This was repeated in this laboratory and the value 204.2 was obtained.

to about 48 g. remained. This material was fractionally crystallized from absolute alcohol and from ethyl acetate.

It consisted in part of a crystalline mixture of phytosterols and also of an oily fraction which remains in the mother liquors after the separation of the less soluble phytosterols. A fraction of these melting at 134–135° was analyzed.

Calc. for $C_{27}H_{46}O \cdot H_2O$: H_2O , 4.8; found: H_2O , 4.7.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9; found: C, 83.8; H, 11.9.

As the melting points of the various fractions were not constant, the entire fraction was acetylated and 13.2 g. of the acetates were obtained. When tested for the presence of stigmasterol by the method of Windaus and Hauth¹ it gave negative results. The remaining 10 g. were fractionally crystallized from ethyl acetate. By this means two fractions were finally separated, the less soluble melting at 131.5–132°, and the other melting at 118–120°. The former separated in plates while the lower melting compound formed needles. The acetate melting at 131.5–132° was analyzed.

Calc. for $C_{29}H_{48}O_2$: C, 81.2; H, 11.3; found: C, 81.0; H, 10.9.

When hydrolyzed it proved to be a mono-acetate. 0.3904 g. yielded acetic acid equivalent to 11.1 cc. 0.1 N KOH while the calculated volume required by the formula $C_{27}H_{46}OCOCH_3$ is 9.2 cc.

The regenerated phytosterol crystallized from ethyl acetate formed well defined plates that melted at 154.5–156.5°. It was dried at 110°.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9; found: C, 83.7; H, 11.7.

0.3446 g. of the anhydrous phytosterol made up to 20 cc. with chloroform showed a rotation of -1.46° in a 2 dcm. tube, whence $[\alpha]_D^{20} = -42.2$.

The more soluble fraction of the acetate when hydrolyzed yielded a phytosterol that melted at 136–137°. It was dried at 110°.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9; found: C, 83.8; H, 11.8.

In the course of this fractional crystallization, by means of which the above phytosterol acetates were separated, we obtained a large intermediate fraction, which yielded a series of crystallizations wherein the melting point ranged from 121.5–126°. Whether or not this contained a third isomer such as sitosterol was not established. From the fraction of the acetates melting at 126° a further quantity of the phytosterol melting at about 155° could be prepared.

The syrupy mother liquor remaining after these substances had been isolated was freed from alcohol and subjected to a fractional distillation. It passed over between 210° to 310° at 20 mm. Most of the oil distilled at 240–290°. The fractions were thick, sticky, oils which did not solidify upon cooling.

¹ Ber., 39, 4378 (1906); 40, 3681 (1907).

The Ether Extract of the Resin.—Upon concentrating the ethereal solution a quantity (0.4 g.) of material separated which gave the color tests characteristic for phytosterolins. It was purified by recrystallization from dilute pyridine and melted and decomposed at 280–290°.

Calc. for $C_{27}H_{46}O_2$: C, 72.3; H, 10.2; found: C, 72.4; H, 10.3.

The phytosterol glucoside was converted into an acetate which melted at 163–164°.

The ethereal solution from which this compound had separated was extracted with solutions of ammonium carbonate, sodium carbonate, and potassium hydroxide. The last named solution dissolved most of the material, but the further examination of both the potassium hydroxide solution and of the ether failed to yield any crystalline substances.

The Chloroform Ethyl Acetate, and Alcoholic Extracts of the Resin, were examined in an exhaustive manner but nothing could be isolated.

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THE QUANTITATIVE DETERMINATION OF THE AMINO ACIDS OF FEEDING-STUFFS BY THE VAN SLYKE METHOD.

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Received April 27, 1915.

Studies relating to the amino-acid content of isolated proteins are of fundamental importance in revealing the character of the chemical processes involved in nutrition and in determining the relative nutritive value of the different proteins. The qualitative and the quantitative amino-acid content of most, if not all, of the forty or fifty natural proteins that have been isolated has been determined by such methods as are now available for such work. However, the quantitative amino-acid content of the mixed proteins of our feeding-stuffs is still entirely unknown. It is desirable, if possible, to determine the amino-acid values of feeding-stuffs, since practical animal husbandry men must always deal with certain mixtures of proteins and protein derivatives as they are found in the naturally occurring feeds.

It is at present impossible to calculate the amino-acid content of feeding-stuffs from the amino-acid content of the isolated proteins for two reasons: first, all of the proteins of any one of the common feeding-stuffs, except milk, have not as yet been isolated in a pure state; and second, there are as yet no methods available for the quantitative separation and determination of the proteins of feeding-stuffs, although some of the main proteins of a number of the feeding-stuffs have been qualitatively separated.

As T. B. Osborne has clearly pointed out, it is quite important for us to know, finally, if possible, the proportion of each type of protein con-

tained in feeding-stuffs, yet, this is probably not so essential as a knowledge of the amino-acid content since the nutritive values of the mixed proteins of feeding-stuffs are ultimately determined by their amino-acid content and not by the proportion of the various proteins which they contain. If the amino acids can be determined without first isolating and purifying the proteins of the feeding-stuffs, the desired information can be obtained much more readily.

With the object of determining quantitatively the amino acids of feeding-stuffs we undertook to apply the Van Slyke¹ method which he and other investigators have so successfully used in the determination of the chemical groups characteristic of the different amino acids of proteins. In doing this work we have followed in considerable detail the Van Slyke method, with the exception that the quantities of the feeding-stuff taken for the hydrolysis have necessarily been larger than the amounts of the protein material used by Van Slyke.

The results so far obtained are given in condensed form in Tables I and II. The duplicate or triplicate results reported for the same feeding-stuff were obtained from the hydrolysis of two or three different portions of the same sample of cottonseed meal, tankage and alfalfa hay.

The results of the determinations given below indicate that the Van Slyke method for the determination of the chemical groups characteristic of the amino acids can be applied directly to the quantitative determination of amino acids of feeding-stuffs with at least a fair degree of accuracy.

TABLE I.—THE QUANTITATIVE DETERMINATION OF THE AMINO ACIDS OF FEEDING-STUFFS.

Results expressed in per cent. of the total nitrogen of the feeding-stuff.

Feeding-stuffs.	Ammonia N.	Mel-anine N.	Arginine N.	Cystine N.	Histidine N.	Ly-sine N.	Amino N in filtrate from bases.	Non-amino N in filtrate from bases.	Total N by summation.
Cottonseed meal...	10.46	7.65	19.33	0.62	5.28	5.81	42.61	5.74	97.50
" " ...	10.30	7.78	19.49	0.65	4.90	4.33	42.04	5.30	94.79
" " ...	10.59	7.91	19.74	0.67	6.23	4.21	43.80	5.26	98.41
Average.....	10.45	7.78	19.52	0.65	5.47	4.78	42.82	5.43	96.90
Tankage.....	6.52	4.40	14.38	1.27	5.15	7.52	52.36	7.27	98.87
"	6.56	4.50	14.18	1.24	4.76	7.64	52.57	7.17	98.62
"	6.66	4.30	13.88	1.32	4.91	7.28	52.24	7.38	97.97
Average.....	6.58	4.40	14.15	1.28	4.97	7.48	52.39	7.27	98.49
Alfalfa hay.....	8.46	15.54	7.72	0.79	7.39	4.08	43.88	10.14	98.00
" "	8.42	16.03	7.64	0.97	7.49	4.12	44.15	9.43	98.15
Average.....	8.44	15.79	7.68	0.88	7.44	4.10	44.02	9.79	98.08

¹ D. D. Van Slyke, *J. Biol. Chem.*, 9, 185 (1911); 12, 275 (1912); 16, 121 (1913-14).

TABLE II.—THE QUANTITATIVE DETERMINATION OF THE AMINO ACIDS OF FEEDING-STUFFS.

Results expressed in per cent. of the feeding-stuff.

Feeding-stuffs.	Ammonia N.	Mel- anine N.	Argin- ine N.	Cys- tine N.	Histi- dine N.	Ly- sine N.	Amino N in filtrate from bases.	Non- amino N in filtrate from bases.	Total N by summa- tion.
Cottonseed meal	0.702	0.514	1.298	0.041	0.355	0.390	2.862	0.385	6.547
" "	0.692	0.522	1.309	0.044	0.329	0.291	2.824	0.356	6.367
" "	0.711	0.531	1.326	0.045	0.418	0.283	2.941	0.353	6.608
Average.....	0.702	0.522	1.311	0.043	0.367	0.321	2.876	0.365	6.507
Tankage.....	0.653	0.440	1.439	0.128	0.516	0.753	5.238	0.729	9.896
"	0.657	0.451	1.420	0.124	0.477	0.765	5.264	0.718	9.876
"	0.667	0.430	1.390	0.132	0.492	0.729	5.213	0.739	9.782
Average.....	0.659	0.440	1.416	0.128	0.495	0.749	5.238	0.729	9.851
Alfalfa hay.....	0.221	0.408	0.203	0.021	0.194	0.107	1.160	0.248	2.553
" "	0.222	0.421	0.201	0.023	0.197	0.108	1.153	0.266	2.593
Average.....	0.222	0.415	0.202	0.019	0.196	0.108	1.157	0.257	2.573

At present we are unable to explain the consistently low percentages of the nitrogen of feeding-stuffs recovered as compared with the results obtained by Van Slyke for isolated proteins. This question is now being further studied in detail. A study is also being made of the free amide and the free amino acids of feeding-stuffs, with the object of determining to what extent, if any, the so-called nonprotein nitrogenous substances affect the quantitative determination of the amino acids of feeding-stuffs by the Van Slyke method.

It is evident from the results given in the above tables that there are marked differences in the amino-acid content of the three feeding-stuffs here reported. Hence, it is logical to suppose that the feeds would have a widely different nutritive value, particularly as supplements to such feeds as corn.

The quantitative determination of the amino acids of feeding-stuffs together with the aid of the rapidly increasing evidence on the nutritive functions of the amino acids will make it possible to extend our present knowledge of feeding-stuffs along the following lines:

First, the results will make it possible to calculate balanced rations from the standpoint of their amino-acid content that will be most efficient for the maintenance, the growth, and the fattening of farm animals.

Second, the results will be helpful in the interpretation of the results of past and future feeding experiments.

Third, the results should lead to a method of applying the recent and the fast accumulating results, as to the nutritive value of the amino acids, to the economic and nutritive valuation of the common feeding-stuffs.

Fourth, the results will make it possible to plan and to make feeding experiments with farm animals with the natural mixtures of proteins as they occur in common feeding-stuffs, that will aid in the determination of the relative efficiency of the proteins of different feeding-stuffs for the maintenance, the growth, and the fattening of farm animals.

The determination of the amino acids of feeding-stuffs will be continued by this department. The results for a number of other feeding-stuffs will be published in the near future. The quantitative determination of the amino acids of the roughages, such as the hays, corn fodder, corn silage, the grasses, the straws, and the roots and tubers will be especially valuable and interesting since as yet we have no knowledge of the nature of the proteins of these feeding-stuffs.

A study of methods for the separation and the quantitative estimation of the amino acids included in the groups represented by the amino nitrogen and the nonamino nitrogen in the filtrate from the bases obtained in the Van Slyke method has also been undertaken in this connection.

URBANA, ILL.

NEW BOOKS.

Elementary Chemical Microscopy. By ÉMILE MONNIN CHAMOT, Professor of Sanitary Chemistry and Toxicology, Cornell University. xiii + 410 pp.; 130 figs. New York: John Wiley & Sons, Inc. Price, \$3.00 net.

Notwithstanding the ever-increasing demands on the analytical chemist, the system of instruction in many American institutions has hardly changed since the days of Bunsen and Fresenius. Microscopic methods have been quite generally neglected. Most analysts approach the stage of the microscope with the fright of an amateur performer which is in striking contrast to the confident enthusiasm of Professor Chamot's students.

Since, at best, the laboratory work in analytical chemistry in the usual college course is only a start on the right road the student who has thorough grounding in several lines of attack is at a great advantage. With this equipment he can be left to schoolmaster Experience for the rest of his training.

Professor Chamot in his book has generously extended to students outside of his university and to those in practical work the advantages hitherto enjoyed only by his students. If the chemist is not called on to use the book in his college work he will at least find it useful in after-life.

The term "Chemical Microscopy" as used in the title is particularly fortunate and is much to be preferred to "Micro-chemistry" which suggests that the phenomena observed under the microscope are different from those seen with the naked eye.

Chapters I to XIII inclusive are devoted to the microscope, microscopic

accessories and technique. Far from being tedious pages culled mostly from manufacturers' catalogs, this part of the book is practical and concise, containing a vast amount of accumulated information found elsewhere only after careful search, if indeed at all. The directions for determining the crystallographic system, index of refraction, melting and subliming points will be found useful to analytical and synthetical chemists alike.

In Chapter XIV are given the characteristic reactions of 23 cations and 27 anions, being those ordinarily included in works on analytical chemistry. The descriptions are detailed and more distinctly chemical than in foreign works on microscopic qualitative analysis.

Chapter XV on the preparation of opaque objects will be of special value to those undertaking petrographic and metallographic work.

The author has not invaded the field of vegetable and animal histology. In a book of this character it is doubtless wise to avoid morphology of tissues, but a short chapter on the characteristic reactions of the common constituents of plants and animals, such as starch, sugars, proteins, fats, tannin, etc., might prove a useful addition without greatly increasing the size of the book. However, the fact that the author is a master of these as well as inorganic reactions suggests that he has good reasons for keeping within the present bounds.

The clearly written text, the remarkably well executed illustrations and the novelty of the subject should prove a lure to English-speaking chemists and induce not a few to follow up chemical microscopy as a very useful specialty.

A. L. WINTON.

Moderne Kriminalistik. By A. HELLWIG. 104 pp.; illustrated. Leipzig: B. G. Teubner. 1914. Price, 1.25 Mk.

This little book treats in a general way of the various methods of tracing crime and criminals followed at the present time. Among other things discussed we find references to the aid which may be secured through chemistry and microscopy in several classes of criminal inquiries. Aside from this, the book contains nothing of chemical interest.

J. H. LONG.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

I. NOTES ON SODIUM COLUMBATES. II. THE ATOMIC WEIGHT
OF COLUMBIUM.

BY EDGAR F. SMITH AND WALTER K. VAN HAAZEN.

Received June 8, 1915.

I. Notes on Sodium Columbates.

Little is known concerning the constitution of the columbic acids, hence their salts, the columbates, are usually expressed in the old dualistic form. Thus the general formula of the sodium columbates may be written: $x\text{Na}_2\text{O} \cdot y\text{Cb}_2\text{O}_5 \cdot z\text{H}_2\text{O}$. If we are to accept all the various ratios recorded in the literature, $x:y$ may vary from 4 to 0.25.¹ However, many of these salts were undoubtedly derived from impure material, while others were probably mixtures that happened to approach atomic ratios. The present investigation was restricted to the 7:6 and 1:1 ratios.

The former ratio was fully established by Bedford,² working in this laboratory, and confirmed by Balke and Smith.³ They prepared the salt $7\text{Na}_2\text{O} \cdot 6\text{Cb}_2\text{O}_5 \cdot 31\text{H}_2\text{O}$ by different methods which had already been used by H. Rose, Hermann, and others, but had failed to give this particular salt. The 1:1 ratio had also been reported by Rose, but rested on questionable evidence, as was pointed out by Balke and Smith. These

¹ Abegg, "Handbuch," III, 3.

² THIS JOURNAL, 27, 1216 (1905).

³ *Ibid.*, 30, 1644 (1908).

investigators allowed the mother liquors from the 7:6 salt to evaporate spontaneously and obtained a well-defined salt having the composition $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_6 \cdot 7\text{H}_2\text{O}$ (metacolumbate). They also determined its crystal habit, which has been very helpful in the present work.

The simple ratio and definite crystalline form of the 1:1 salt suggested its use for a redetermination of the atomic weight of columbium. Before this was undertaken, however, it seemed desirable to ascertain whether this compound could really be obtained sufficiently pure; that is to say, whether it was liable to be contaminated by the 7:6 salt, whether it was capable of recrystallization; and finally, as it was to be obtained from the mother liquor of another salt, whether any definite relation existed between these two salts.

For this part of the investigation some pure potassium oxyfluocolumbate was available which had been prepared, in this laboratory, by W. H. Chapin, in connection with his work on tantalum.¹ A quantity of this salt, dissolved in hot water, was mixed, in a large platinum dish, with three times its weight of pure sodium hydroxide (from sodium) dissolved in the least possible amount of water. This represents a large excess of alkali, but, as several failures indicated, this amount was practically necessary for the end in view. The heavy, white precipitate, which was insoluble in the excess of sodium hydroxide, was washed by decantation, filtered by suction, and washed with small quantities of cold water until a considerable portion of the columbate had been carried into the filtrate; this was noticed by a fresh precipitate being formed in the original filtrate containing the excess of alkali. The washed precipitate was then dissolved in boiling water and allowed to crystallize; this gave the 7:6 sodium columbate. Several preparations of the salt were made by this method, and it was soon noticed that the yield was conditioned by the amount of alkali used and the thoroughness exercised in washing the original precipitate. That is to say, a proportion of alkali smaller than that indicated above, followed by a very thorough washing, would produce little or no 7:6 salt; whereas a large excess of alkali and a rather superficial washing would increase the yield. This seemed to indicate that the formation of this salt was facilitated by a little free alkali in solution. This view was also supported by the fact that the crystallization could be hastened by the addition of a little sodium hydroxide, or carbonate, to a solution of the well-washed precipitate. The significance of this circumstance will appear below.

The 7:6 salt was recrystallized from boiling water and the mother liquor combined with that from the preceding crystallization. The combined liquids were allowed to evaporate spontaneously in a large platinum dish. After several weeks, large and well-defined crystals

¹ Thesis, Univ. of Penna., 1909.

appeared; they resembled those obtained by Balke and Smith, and proved to be the 1:1 salt.

Analysis: 0.4719 g. of salt lost 0.1292 g. on ignition; 0.6604 g. of salt gave 0.3889 g. of columbic oxide, and 0.2046 g. of normal sodium sulfate, or:

		Calculated.	Found.
Na_2O	62	13.65%	13.53%
Cb_2O_5	266.2	58.61	58.80
$7\text{H}_2\text{O}$	126	27.74	27.59
	<hr/>	<hr/>	<hr/>
	454.2	100.00%	99.92%

In analyzing these columbates the columbium was precipitated from a hot solution of the salt by the addition of dilute sulfuric acid. The filtrate was evaporated to dryness and ignited so as to form normal sodium sulfate. Only a very slight excess of the acid was used, otherwise much columbium was carried into the sodium sulfate.

Difficulty was encountered in attempting to recrystallize the 1:1 salt from water; usually the product was partly amorphous and far from uniform. Only one attempt was successful. In this instance the salt was dissolved in water of about 65°, the solution protected from the carbon dioxide of the air, and allowed to crystallize, under atmospheric pressure, over concentrated sulfuric acid.

Analysis of the recrystallized salt: 0.4850 g. of salt lost 0.1357 g. on ignition; 0.5574 g. of salt gave 0.3264 g. of columbic oxide, and 0.17733 g. of sodium sulfate, or:

		Calculated.	Found.
Na_2O	62	13.65%	13.58%
Cb_2O_5	266.2	58.61	58.56
$7\text{H}_2\text{O}$	126	27.74	27.98
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	454.2	100.00%	100.12%

The following data may serve to point out the chief differences between the 7:6 and the 1:1 salt:

The 7:6 salt crystallizes in definite needles or slender prisms, often microscopic in size. It is difficultly soluble even in hot water. Upon ignition it becomes lemon-yellow in color, the latter deepening with increase of the temperature; it becomes white again on cooling. When heated it begins to cake somewhat, but does not melt, even at 1000°. The ignited mass appears to be insoluble in water, but part of its alkali splits off, leaving the 1:1 salt, according to the reaction:



As the sodium hydroxide seems to exert a solvent action on the metacolumbate produced, this reaction was not very sharp when the mass was extracted with water alone. A somewhat better result was obtained by extracting with dilute hydrochloric acid. Even in this case a small amount of columbic hydroxide appeared in the filtrate upon the addition

of ammonium hydroxide; it was neglected, and this fact probably accounts for the low result.

Analysis: 1.5042 g. of 7:6 salt lost 0.4124 g. on ignition; another sample of the same salt weighing 1.3953 g. was extracted with dilute hydrochloric acid; the residue weighed 1.0454 g.

	Calculated.	Found.
12NaCbO_3 (insoluble).....	76.06%	74.92%
$1\text{Na}_2\text{O}$ (soluble).....	2.39
$31\text{H}_2\text{O}$	21.55	21.52
	<hr/> 100.00%	<hr/>

The 1:1 salt, on the other hand, crystallizes in well-defined, short, stout, triclinic¹ crystals which, under favorable conditions, may grow to be 6–7 mm. in length. When allowed to crystallize under the microscope, the salt makes its appearance in diamond-shaped, or "coffin"-shaped forms, differing very distinctly from the needles of the former columbate. It is much more soluble than the 7:6 salt. It carries seven molecules of water of crystallization, the greater part of which (about 5 molecules) can be driven off on the steam bath. On ignition it also becomes yellow, but does not cake, even at 1000°. Strangely enough the crystals, when heated, do not fall to a powder, but merely shrink, retaining their original form and becoming quite hard. Water has no perceptible action upon this ignited mass and remains neutral in reaction; this test easily distinguishes this salt from the former.

As Bedford² has shown, the 7:6 salt can be thrown out of solution by alcohol. It was thought that the metacolumbate might be precipitated in a similar manner and thus be purified. However, when a solution of the 1:1 salt was treated with an excess of alcohol a mixture was precipitated. When absolute alcohol was added slowly, with constant stirring, in quantities sufficient to increase the original solution by one-third, a crystalline precipitate appeared which, under the microscope, resembled the 7:6 salt. Its analysis gave the following results:

0.2408 g. of salt lost 0.0523 g. on ignition; 0.2771 g. of salt gave 0.1702 g. of columbic oxide, and 0.1063 g. of sodium sulfate; or:

	Calculated for		Found. Salt by alcohol.
	1:1 salt.	7:6 salt.	
Na_2O	13.65%	16.76%	16.75%
Cb_2O_6	58.61	61.69	61.53
H_2O	27.74	21.55	21.72
	<hr/> 100.00%	<hr/> 100.00%	<hr/> 100.00%

The close summation is, of course, merely accidental. The result ad-

¹ Balke and Smith, *loc. cit.*, p. 1651.

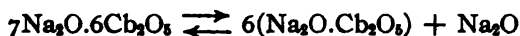
² THIS JOURNAL, 27, 1217 (1905).

mits of no doubt that alcohol really produced this peculiar change, which, in its simplest form, may be expressed as follows:

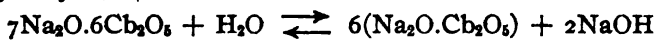


In other words, in addition to the precipitate, columbic acid, or more likely, an acid columbate was probably formed which was not precipitated by a moderate amount of alcohol. An excess of the latter precipitated practically everything in solution and thereby produced the mixture referred to above. Some other neutral substances, likewise, seem to precipitate the 7:6 salt, the less soluble compound, from a solution of the meta-salt. Thus a solution of sodium chloride produces a crystalline precipitate resembling the 7:6 salt; its composition, however, was not determined.

From the preceding observations it may safely be concluded that the two sodium columbates discussed, the 7:6 and the 1:1 salts, are mutually convertible, and that their relation may be expressed by the reversible reaction:



In water solution this change must be assumed to take the form of a partial hydrolysis, as follows:



This suggested the use of carbon dioxide for hastening the reaction to proceed from left to right. When carbon dioxide was passed through the solution of the 7:6 salt the hydrolysis seemed to go beyond the 1:1 stage. However, when the solution was slowly condensed on the water bath, while an atmosphere of carbon dioxide was maintained *above* the liquid, a good yield of the 1:1 salt could be obtained. This method was finally used in the atomic weight determinations and will be mentioned again in Section II. It may be added that carbon dioxide does not, at any time, produce a turbidity in a solution of a pure columbate, even when the latter is exposed to the gas for many hours. This fact seems to prove conclusively that Rose's columbates must have been contaminated by other elements (probably by titanium or tantalum, or both), for he asserts that he obtained a gelatinous precipitate by¹ the action of carbon dioxide.

The mother liquors from the 1:1 salt may yield still other columbates, more acid than those discussed. However, as the acid content increases, the solubility seems to increase also, and these salts are crystallized with difficulty. In one instance the mother liquor from the 1:1 salt was allowed to evaporate spontaneously. An analysis of the resulting crystals indicated a salt between the ratios 3:4 and 4:5. It may be interesting to note that in another case the mother liquor from the 1:1 salt was evaporated to

¹ *Pogg. Ann.*, 136, 367 (1869).

dryness, ignited, and fused with sodium carbonate. A fresh crop of 7:6 salt was obtained, allowed to remain, as crystals, in the liquid, and the whole exposed to the action of carbon dioxide as explained before. Excellent crystals appeared after concentrating and cooling; they proved to be the 1:1 salt. Analysis:

0.5489 g. of salt lost 0.1526 g. on ignition; 0.4660 g. of salt gave 0.2732 g. of columbic oxide, and 0.1422 g. of sodium sulfate; or:

	Calculated for 1:1 salt.	Found.
Na ₂ O.....	13.65%	13.42%
Cb ₂ O ₅	58.61	58.63
7H ₂ O.....	27.74	27.80
	<hr/> 100.00%	<hr/> 99.85%

The experimental data seem to prove that the 7:6 and 1:1 sodium columbates are two distinct and well-defined salts, and that they are mutually convertible. Undoubtedly other ratios do exist. It seems reasonable to suppose, however, that some of the rather improbable ratios recorded in the literature, and the failure of some chemists, like Marignac,¹ to obtain any definite sodium columbates, are to be attributed to the susceptibility of these salts to progressive hydrolysis together with the influence of carbon dioxide and free alkali, all of which factors might easily lead to the production of mixtures.

II. The Atomic Weight of Columbium.

The earliest determinations of the atomic weight of columbium are due to Rose, Hermann, and Blomstrand; the values obtained by these chemists are, today, of little more than historical interest. The researches of Marignac led to the first acceptable figure, about 94, which stood unchallenged for over fifty years. These earlier determinations need not be discussed here. A brief criticism of them may be found in Abegg's "Handbuch;" they are also commented upon by Balke and Smith in the paper "Observations on Columbium."² The only modern determination was made by the last-named investigators; they obtained an average of 93.50 for this element.

Balke and Smith made use of the ratio 2CbCl₅:Cb₂O₅, established by the hydrolysis of the pentachloride. Their columbium was undoubtedly of high purity; however, certain other factors may have influenced the ratio. Thus, for example, the pentachloride is liable to retain traces of oxychloride. Furthermore, the residual oxide may have retained chlorine; this seems quite probable from the recent work of Sears and Balke³ on the atomic weight of tantalum by a similar method. Both of these factors would tend to give too high an atomic weight. Finally, a slight volatiliza-

¹ *J. Chem. Soc.*, 97, 453 (1866).

² *THIS JOURNAL*, 30, 1644 (1908).

³ *Ibid.*, 37, 840 (1915).

tion of columbium may have taken place, for, according to Hall and Smith¹ columbic oxide is volatile with hydrochloric acid gas; this would tend to lower the atomic weight. If the latter effect influenced the ratio, in addition to the first two, it is idle to conjecture as to which of these factors finally turned the balance. In any case, the value obtained by this method must be looked upon as somewhat uncertain, and a new determination by an entirely different method did not seem out of order.

It was decided to use sodium metacolumbate as a starting-out material, for the observations recorded in the first part of this paper point to this as the only sodium salt at all desirable for the end in view. As Hall² had been able to decompose native columbates by means of sulfur monochloride, it was to be expected that this reagent would effect the decomposition of a sodium columbate also, thus leading to the ratio $\text{NaCbO}_3 : \text{NaCl}$. This was found to be actually the case, although the method required certain modifications. These will receive due notice after a brief description of the preparation and purification of the chief reagents used.

Some crude potassium fluocolumbate was on hand; it had originally been prepared by Hall³ from South Dakota columbite. This salt was purified by methods that have been in use in this laboratory for some time and have been found to give pure columbium.⁴ Suffice to say that this double fluoride was recrystallized five times from rather strong (1:1) hydrofluoric acid which had been redistilled for the purpose from potassium fluoride and a little silver phosphate. The salt was then converted into the oxyfluoride, and baked and recrystallized alternately; this process was also repeated five times. Platinum vessels and centrifugal draining were used throughout. The salt was then decomposed with concentrated sulfuric acid which had been redistilled from a retort of hard glass. The resulting columbic hydrate was thoroughly washed, first with water, and finally with a dilute solution of ammonium carbonate. The latter had first been digested with a little pure columbic hydrate and filtered; it was then used as indicated. After a prolonged washing the columbium hydroxide was obtained free from sulfates. This preparation was proved to be free from titanium by the salicylic acid reaction:⁵ the absence of tantalum had been established by the well-known crystallization test.⁶

Sodium carbonate was purified in the following manner: A good c. p. grade was fused with a little pure, precipitated calcium carbonate; traces of silica, iron, etc., were thus rendered insoluble. The melt was disintegrated with water, filtered, and treated with carbon dioxide. The sodium

¹ *Proc. Am. Phil. Soc.*, 44, 197 (1905).

² Thesis, Univ. of Penna., 1904.

³ Hall and Smith, *THIS JOURNAL*, 27, 1369 (1905).

⁴ *Ibid.*, see also Balke and Smith, *loc. cit.*

⁵ J. H. Müller, *THIS JOURNAL*, 33, 1508 (1911).

⁶ *Proc. Am. Phil. Soc.*, 44, 180 (1905); *THIS JOURNAL*, 27, 1372 (1905).

bicarbonate produced was drained by centrifugal force and reprecipitated twice as the acid salt; it was now ready for use.

For the preparation of the metacolumbate the ignited columbic oxide was mixed with five to six times its weight of the sodium bicarbonate, ignited gently, and finally fused. Contrary to some statements a perfectly clear fusion can be brought about in this manner. After disintegrating the melt with water, sodium columbate remained as a heavy, white precipitate, insoluble in the excess of alkali. This was washed as indicated in Section I. It may be mentioned that no trace of sulfuric acid could be detected in this alkaline filtrate, showing that the columbic oxide had been free from this contamination. The well-washed mass thus obtained was crystallized, in a large platinum dish, from boiling water; this gave a small amount of 7:6 salt. The mother liquor from the latter was placed in a platinum dish and slowly condensed on the water bath. In the meantime an atmosphere of carbon dioxide was maintained above the liquid. The solution was stirred frequently, and a drop removed from time to time and allowed to crystallize under the microscope. Finally nothing but the characteristic, well-defined crystals of the 1:1 salt were noticeable when the drop had evaporated almost to dryness. By this time the solution had been condensed to about one-half its original volume. The liquid, which was entirely clear, was then cooled, inoculated with a trace of 1:1 salt from a previous preparation, and allowed to crystallize. Small but excellent crystals of the 1:1 salt were obtained. Under the microscope they appeared entirely uniform and free from inclusions or alterations of any sort. The crystals were washed several times with small quantities of cold water, being drained centrifugally after each washing. They were finally dried in air free from carbon dioxide. Several attempts were made to recrystallize this salt from water, but with little success. The product always suffered, except in one case, from one defect or another. It was finally decided to use the well-washed salt without recrystallizing.

The columbium of this salt must have been of high purity. It seemed possible, however, that the preparation might be contaminated with traces of either an acid columbate, or with free alkali, the latter being present as such or resulting from a trace of 7:6 salt on ignition. (See Section I.) The presence of an acid columbate was highly improbable on account of its greater solubility, and because of the care exercised in crystallizing the salt. That the amount of free alkali, if present at all, must have been exceedingly small seems to be indicated by the following tests: A powdered and ignited sample of the metacolumbate, weighing about one gram, was extracted with a cubic centimeter of hot water; the extract had no effect on very sensitive litmus paper. When a similar portion was boiled up with a small quantity of water, a drop of phenol-

phthalein would only produce an extremely faint pink color; no color was noticeable in the cold. Another sample of the ignited salt was extracted with dilute alcohol, the extract acidified with hydrochloric acid and evaporated to dryness. When water was added and the liquid tested with silver nitrate only a very faint opalescence appeared. Undoubtedly traces of the salt itself dissolved under these conditions, hence the degree of opalescence could not serve as an indirect measure for any free alkali in the salt. The tests seem to show, however, that the metacolumbate must have been reasonably free from traces of 7:6 salt and from uncombined alkali.

The sulfur monochloride was prepared by the action of dry chlorine upon dry, molten sulfur contained in a retort. The sulfur had been re-sublimed for the purpose; the chlorine was generated by the action of pure hydrochloric acid on potassium permanganate. The sulfur monochloride was redistilled twice in a stream of carbon dioxide. In every operation the apparatus used was constructed entirely of glass, with only a few well-ground connections.

The carbon dioxide was generated by the action of hydrochloric acid on white marble. The gas was passed through a large tower containing beads coated with moist sodium bicarbonate, then through a similar tower charged with moist silver carbonate. Several wash-bottles containing glass beads and concentrated sulfuric acid served to dry the gas sufficiently for the purpose. In order to remove any possible traces of acid it was finally conducted over fused, granulated potassium carbonate.

Ordinary distilled water was used in washing the columbium hydroxide. The water used in the subsequent operations had been distilled from alkaline potassium permanganate, then from a small quantity of acid potassium sulphate; the product was redistilled as needed.

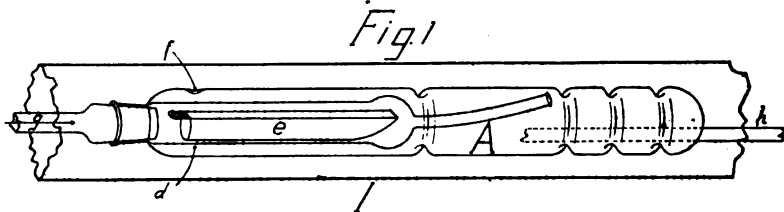
The method proposed for the determination of the ratio consisted essentially in heating the dehydrated metacolumbate in the vapor of sulfur monochloride; columbium was expelled as chloride or oxychloride, while sodium chloride remained behind. Since the air could not be removed completely from the apparatus by the sulfur monochloride alone, carbon dioxide was used for this purpose, serving, at the same time, as a vehicle for the former.

It was soon found that the columbium could not be expelled completely from the columbate, even by a prolonged action of the sulfur monochloride. The residue would finally come to constant weight, it is true, but numerous trials showed that a portion (amounting to several per cent.) of the columbate always remained unaffected, even when the salt had been ground to a fine powder. However, when the residue in the boat was moistened with water, evaporated to dryness, and again

subjected to the action of sulfur monochloride a fresh sublimate of the chloride of columbium would appear.

In this manner the reaction could finally be carried to completion; that is to say, the residue would eventually consist of pure sodium chloride and completely dissolve in water. This seemed to indicate that the difficulty was merely mechanical in nature. At first it was thought that the sodium chloride formed was possibly raised to incipient fusion by the heat of the reaction, and that it thus protected part of the columbate from further action. The true explanation of this difficulty, however, is probably to be sought partly in the molecular magnitude of sulfur monochloride, by virtue of which it diffuses through a porous mass more slowly than, let us say, hydrogen; partly in the fact that sodium chloride has a lower density, in other words, is more voluminous, than sodium columbate and thus may protect the unchanged columbate in the interior of a particle much more effectively than if the respective densities were interchanged. Possibly the carbon dioxide also had a retarding influence. However this may be, evaporation with water proved to be indispensable and gave results which, for completeness, left nothing to be desired.

Evidently an ordinary boat was unsuitable for this treatment and for the evaporation with water. Several devices were tried; they need not be described here, with the exception of the one finally adopted. It gave entire satisfaction, and is shown in Fig. 1.



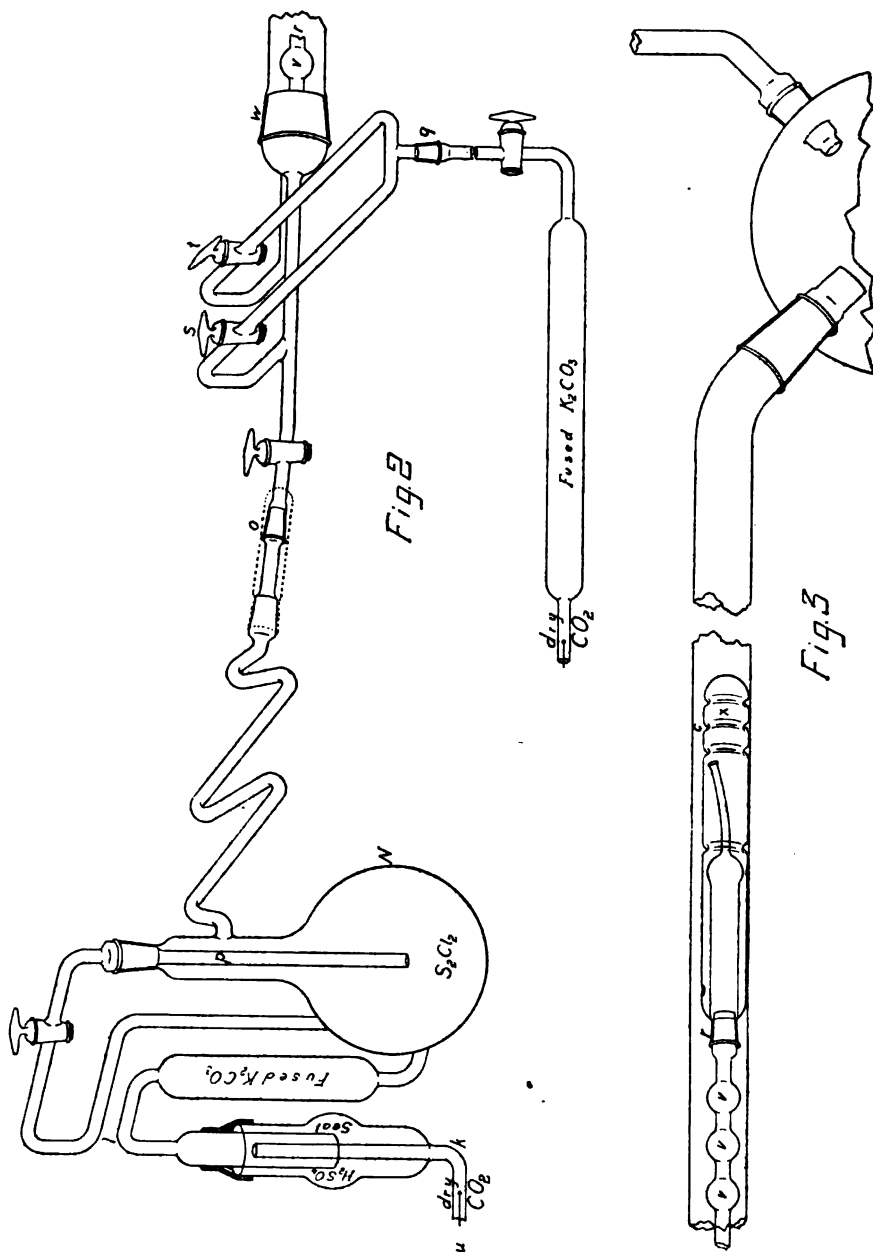
The reaction tube (A) consisted of fused, transparent quartz; it was about 150 mm. long and 18 mm. in diameter. The quartz tube (g) was not ground into (A), but merely formed a smooth contact joint. The inner tube (d) was wide enough to admit a long, narrow platinum boat (e) having convex sides conforming to the tube, so as to increase the capacity. The exit from the reaction tube is indicated at (f), a small circular opening. The columbate, roughly dehydrated in a current of dry air, was put into the boat (e) and the dehydration completed in this apparatus. Carbon dioxide was removed from all air used in drying; this precaution, however, was probably superfluous. The quartz reaction tube was never heated directly. It was supported by a rack made of stout "nichrome" ribbon covered with platinum foil and placed in another quartz tube (I) to which the heat was applied. The temperature was raised gradually until it finally reached 760–800°; it was measured by means of a thermo-

couple, part of which is indicated at (*h*). Although the columbate was infusible, the crystals directly in contact with quartz had a slight corroding action on the latter at elevated temperatures; for this reason the platinum boat was used in the dehydration. During the entire operation a steady stream of dry air entered the tube through (*g*). It has been said before that the salt gives up the bulk of its water of crystallization at a rather low temperature; for the expulsion of the last traces of water, however, a temperature of nearly 800° was found to be necessary. The complete dehydration required at least ten hours of continued heating, usually much longer. It may be stated that the completely dehydrated columbate was remarkably stable toward further ignition. In one instance the perfectly dry salt was ignited again for about ten hours, in the manner indicated; it varied less than 0.02 mg. from the original weight.

In each determination the columbate was dehydrated in this manner until its weight remained practically constant. When this had been accomplished the granular residue (NaCbO_3) was allowed to glide from the platinum boat into the lower compartment of the quartz tube and the boat withdrawn; the exact weight of the columbate was then determined, hence the weight of the boat did not figure in the calculation. The substance was now ready to be acted upon by sulfur monochloride.

The apparatus used for the decomposition of the columbate by sulfur monochloride is sketched in Figs. 2 and 3, with the exception of the carbon dioxide generator and the drying train. It was constructed entirely of glass. All ground connections had been fitted with great care as no lubricant could be used; they were held in position by wire clamps. The diagram needs little explanation. The apparatus could be disconnected by moving the distilling bulb (*N*) in the direction (*o,p*), thereby turning (*l*) about the vertical axis (*k,l*) and the neck of the distilling bulb slightly about its ground-in tube (*p*). The unit (*o,q,r*) could then be removed by turning about the axis (*o,r*). After the introduction of the quartz tube with the weighed anhydrous columbate into the combustion tube the air was displaced by dry carbon dioxide through (*s*) and (*t*). Sulfur monochloride was then driven into the tube by gently heating the distilling bulb and admitting carbon dioxide through (*u*), while (*s*) was turned off. Part of the sulfur monochloride condensed again in (*o,r*) and was driven by a gentle heat into the combustion tube as needed. The bulbs (*v,v,v*), were very useful in preventing liquid sulfur monochloride from reaching the reaction tube and causing spluttering. By this arrangement the flow, of the sulfur monochloride could be regulated at will. In the meantime a constant stream of carbon dioxide entered the combustion tube through (*i*), thus preventing the monochloride and other volatile products from "backing up" and reaching the ground joint at (*w*). The charge was just heated sufficiently to drive the volatile products of the reaction be-

yond the quartz tube; only a moderate heat was required. In spite of the gas "pocket" at (*x*) the reaction proceeded with ease. The connection at (*r*) was similar to the one described in the dehydrating apparatus.



When the reaction had become rather sluggish the supply of sulfur monochloride vapor was cut off, the excess of the latter removed by carbon dioxide, and the tube allowed to cool. The residue in the quartz tube was then covered with a little water containing a drop of pure hydrochloric acid, the tube placed in a suitable test-tube with a loose-fitting lid, the whole supported at an acute angle from the horizontal, and the liquid evaporated in an oven, at $110-120^{\circ}$. At this temperature no ebullition of the salt solution took place and, as several accurate weighings showed, no loss of sodium chloride was occasioned by such an evaporation.

The dry residue was then treated again with sulfur monochloride as before, and again evaporated with water. These operations were repeated until a perfectly clear solution of sodium chloride was obtained in the reaction tube on the addition of water. After that the dry residue was given one more treatment with the monochloride. In this manner the completeness of the reaction could be determined much better than by attempting to reach constancy in weight, for at this stage the sodium chloride retained varying traces of water that were not removed during the subsequent treatment with sulfur monochloride. In almost all cases four evaporations with water were sufficient. In these evaporations the sodium chloride "crept" (usually as far as the middle constriction) and thus exposed the unattacked residue. The lower end of the reaction tube was corrugated, as indicated in the sketch at (c), in order to help distribute the residue and to prevent it from forming a single compact mass; this construction facilitated the reaction considerably.

In some preliminary experiments the quartz tube became slightly etched, particularly when a fairly high heat had been applied to the combustion tube. This was probably due to the action of the finely divided columbate remaining after an evaporation with water. In the final determinations only a gentle heat was applied and the difficulty was entirely overcome, for the tube showed practically no variation in weight. It was also noticed that the presence of the hydrochloric acid in the water minimized this action upon the quartz.

As sulfur dioxide is probably produced in the sulfur monochloride reaction it was to be feared that the residual sodium chloride might be contaminated by sulfite or possibly, in the presence of a trace of air, by sulfate. As a matter of fact, an extremely slight test for sulfuric (or sulfurous) acid was obtained in two preliminary experiments. It was probably due to a trace of air in the apparatus; numerous trials convinced the writers that sulfites (or sulfates) are not normally produced in this reaction. Nevertheless a careful test for sulfuric acid was carried out after the completion of each determination. None was found in the final experiments. This test was made as follows: To the residual sodium chloride, dissolved in water, a drop of hydrochloric acid and a little bromine

water are added. The solution was heated to boiling and tested with barium chloride; it was allowed to stand for at least twelve hours. It may be added that the hydrochloric acid present in the water before evaporation also would have served to destroy any sulfite.

When the reaction in sulfur monochloride had come to an end the sodium chloride had to be dried for the final weighing. This was done by heating the salt, very gently at first, in a current of dry air. The apparatus already described under the dehydration of the columbate was used for this purpose (see Fig. 1). The temperature was raised gradually to the fusion point of sodium chloride; during this operation the mouth of the quartz tube was kept much cooler than the rest. In this manner no volatilization of salt from the tube took place. At least two or three weighings were made until the weight of the sodium chloride had become practically constant.

During the weighings the quartz tube was enclosed in a glass-stoppered tube made of light test-tube glass. In each case the weight was obtained by comparing the apparatus containing the substance, by substitution, with a counterpoise which was an exact duplicate of the former. The two weighing bottles containing the quartz tubes were allowed to cool in a large desiccator and were stoppered under the same atmospheric conditions, just before weighing. A No. 10 Troemner balance was used; it was easily sensitive to 0.02 mg. The weights had been carefully calibrated by the substitution method.

All weighings were reduced to the vacuum standard. The density of the ignited sodium columbate was determined in water and found to be 4.19; that of sodium chloride was assumed to be 2.14; the density of the weights was 8.4. The other constants used are: Cl = 35.46; Na = 23.00; O = 16.00. The results are given in Table I.

TABLE I.—ATOMIC WEIGHT OF COLUMBIUM.

Number of analysis.	(a) Weight of anhydrous NaC ₂ O ₄ in vacuum. Grams.	(b) Weight of NaCl in vacuum. Gram.	Ratio a : b.	Atomic weight of Cb.
1	0.36419	0.12975	2.80686	93.089
2	0.69113	0.24617	2.80753	93.128
3	1.04904	0.37368	2.80732	93.116
4	1.64337	0.58516	2.80841	93.180
5	1.33367	0.47487	2.80849	93.185
6	0.88051	0.31366	2.80721	93.110
7	1.29947	0.46289	2.80730	93.115

Average, 93.13

In analyses 6 and 7 a recrystallized sample of sodium columbate was used which had been prepared from Chapin's double fluoride and pure sodium hydroxide (Hermann's method; see Section I). In view of the fact

that this salt had been prepared by a different method from a different preparation the two results seem to agree tolerably well with the average of the first five. In considering the variation in the series it must be borne in mind that samples 1 to 5 had not been recrystallized on account of the difficulties previously explained; as the columbate tends to hydrolyze in water solution, apparently little is to be gained even by a recrystallization. Although this circumstance may be pointed out as a weakness of the method, it should be borne in mind that practically all columbium derivatives suffer from similar or even more serious defects.

Summary.

(1) The relation existing between the 7:6 and 1:1 sodium columbates has been established; they have been shown to be mutually convertible, and both have been prepared by new methods. Characteristic differences between these salts have been pointed out.

(2) Sulfur monochloride has been used, for the first time, directly for the determination of an atomic ratio; its applicability has been demonstrated. The method and the apparatus devised may be of value in other work.

(3) The atomic weight of columbium, as obtained from the ratio $\text{NaC}_2\text{O}_3 : \text{NaCl}$, was found to be 93.13. Although this figure is considerably lower than the present international value, 93.50, it is hoped that the former will prove more reliable than those recorded heretofore.

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THE EXTRACTION AND SEPARATION OF THE RADIOACTIVE CONSTITUENTS OF CARNOTITE.

By H. M. PLUM.

Received May 6, 1915.

Ever since the discovery of radium by Mme. Curie and the announcements of its wonderful properties, there has been a very great demand for this element. On account of its scientific interest, such extensive investigations have been carried out that the supply of radium at all times has fallen short of the demand. The more recent claim that it has therapeutic value in the treatment of such diseases as cancer has so greatly increased the demand, that the study of the radium-producing ores, along with the best methods of extracting the radioactive material, has become extremely important. In view of these facts it can readily be seen that the demand for radium will be on the increase, and that any research which would point out efficient and practical methods for the recovery of this element will be of both scientific and practical value.

This paper presents the results of a critical investigation, carried out under the direction of Dr. Herbert N. McCoy, of various methods of

treating carnotite with the object in view of extracting not only uranium, vanadium, and radium, but also its other long-lived radioactive constituents, ionium, radium D, radium F, and actinium. It has been established by McCoy,¹ Boltwood² and Strutt,³ that there is a constant ratio between uranium and radium in ores. Consequently, the ores richest in uranium contain most radium. Among the most important of these ores are pitchblende, autenite, chalcocite and carnotite. Of these, until recently, pitchblende has been looked upon as the best source of uranium, the mineral usually containing from 40–90% of uranoso-uranic oxide, U_3O_8 . The great demand for the radioactive elements, however, has nearly exhausted the known deposits of this ore.

The main source of supply for uranium at the present time is carnotite. It is a hydrated vanadate of uranium and potassium,⁴ and usually occurs as a canary-yellow powder disseminated in sandstone. It does not occur, as a rule, in a pure state, but as a mixture of minerals containing—in addition to uranium, vanadium and potassium—varying amounts of silica associated with such elements as barium, calcium, and iron. The principal carnotite deposits are those of Colorado and Utah, where uranium ore is found in far larger quantity than in any other region in the world.

Many of the commercial methods proposed for treating uranium ores, or ores containing both uranium and vanadium, have had as their object the extraction of these elements only, without reference to the recovery of the radium. In such cases the radium has been lost because operators have often not known the methods best suited for obtaining it. A considerable amount of American carnotite has been shipped to Europe. These ores have been purchased mainly for their radium content, and the profit has come largely in connection with the extraction of the radium. Richard B. Moore and Karl L. Kithil,⁵ in a preliminary report on uranium, radium and vanadium, and Siegfried Fischer,⁶ in an article on the carnotite industry, have discussed quite fully the principal methods now in use for treating carnotite.

There are two principal methods of attack: acid processes and basic processes. Three of the former may be mentioned: Fleck's method, which consists in leaching the ore with dilute sulfuric acid; Radcliff's,⁷ in which the ore is fused with sodium acid sulfate; and that of Moore and Kithil who effect a partial solution by treatment with boiling nitric or hydro-

¹ McCoy, *Ber.*, 37, 2641 (1904).

² Boltwood, *Nature*, 70, 80 (1904); *Phil. Mag.*, 9, 599 (1905).

³ Strutt, *Nature*, 69, 473 (1904); *Proc. Roy. Soc.*, (A) 76, 81, 312 (1905).

⁴ Hillebrand and Ransome, *Am. J. Sci.*, 10, 120 (1900).

⁵ *Bulletin* 70, U. S. Bureau of Mines, Denver (1913).

⁶ *Trans. Amer. Electrochem. Soc.*, 24.

⁷ U. S. patent No. 1,049,145 (1913).

chloric acid. Among the basic methods, Bleeker's¹ process consists of roasting the ore with sodium chloride and sodium hydroxide; Fischer's,² of evaporating with caustic soda solution and roasting; while Haynes and Engle³ boil with carbonate of soda.

In most of the recent commercial methods which have had to do with carnotite, the investigators have generally been satisfied to find the best means of extracting vanadium, uranium and radium, without regard to the other radioactive elements. In the present work, in addition to the above, the aim has been to follow the other long-lived radioactive elements and to find means of recovering them also.

The ore used in these experiments represented the concentrates from a Colorado carnotite.⁴ It was in a very finely divided form, dark in color, and had been thoroughly mixed in the process of concentration. This concentrate contained approximately 6% of vanadium, 4% of uranium, and 4% of iron. There were only small amounts of barium and lead in the ore, the barium radium sulfate from one kilogram of carnotite weighing about 7 g. The rare earths were lacking and very little, if any, thorium could be detected.

The analysis of the concentrate was made in several ways; the simplest and most satisfactory method consisted in boiling 5 g. of material with a large excess of concentrated nitric acid for about an hour, by which time complete decomposition had taken place. In case vanadium was to be determined, the nitric acid was completely expelled by evaporation to fumes with an excess of sulfuric acid. Water was added and the whole boiled for some time with a large excess of sodium carbonate solution and filtered. The insoluble residue, consisting of the carbonates and hydroxides of iron, etc., was dissolved in hydrochloric acid and again treated with sodium carbonate solution and filtered, and this filtrate added to the main filtrate. This solution now contained all the uranium and vanadium but was free from iron. It was acidified, boiled to expel carbon dioxide, and made alkaline with sodium hydroxide (free from carbonate). The uranium was precipitated as yellow sodium uranate while the vanadium remained in solution as easily soluble sodium vanadate. In case all the vanadium was not present in the pentavalent form, the addition of a little bromine water to the alkaline solution completed the oxidation and rendered the vanadium readily soluble in the sodium hydroxide, thus giving an easy and complete separation of the former from the uranium. The precipitate of sodium uranate was dissolved in sulfuric acid, reduced

¹ U. S. patent No. 1,015,469 (1912).

² U. S. patent No. 986,180 (1911).

³ U. S. patent No. 808,839 (1905).

⁴ This material was furnished by Mr. J. M. Flannery, president of the Standard Chemical Company of Pittsburgh, to whom I wish here to express my thanks for his generosity.

with zinc and titrated with standard permanganate.¹ The mean of concordant analyses was 4.27% uranium. Vanadium was determined in the filtrate from the sodium uranate by acidifying with sulfuric acid, boiling to expel bromine, reducing with sulfur dioxide and then titrating with standard permanganate after freeing the solution from the excess of sulfur dioxide. The average of the results gave 5.5% vanadium.

The total activity of this ore was calculated from the percentage of uranium it contained. According to the method used by McCoy,² 1 g. of an ore containing 4.27% of uranium made into a very thin film, should show a total α -ray activity 1.94 times our standard, which was a thick film of U_3O_8 of 35.41 sq. cm. area. The distribution of this activity, as calculated from the ranges of the radioactive elements on the assumption³ that the intensity of activity is proportional to $R^{1/4}$ (R = range), gave the following results for 100 g. of our ore, for which the total activity should be 194 times that of the U_3O_8 standard:

Element.	Range.	Calculated activity ($R_a = 1$).	Distribution of activity from 100 g. ore.
Uranium 1.....	2.50	0.831	36.3
Uranium 2.....	2.90	0.917	
Ionium.....	3.00	0.938	19.5
Radium.....	3.30	1.000	105.5
Radium Em.....	4.16	1.170	
Radium A.....	4.75	1.275	
Radium C.....	6.94	1.640	
Radium F.....	3.77	1.090	22.6
Actinium and its active products.....			11.0
Total.....			194.9

The activity of actinium was calculated from Boltwood's determination of the activity due to actinium in uranium minerals.⁴ The above figures were used as the basis for finding the percentage of recovery of the different radioactive elements in the experiments carried out in this work. In the case of uranium, however, the percentage of recovery of that element was found directly by analysis, while with radium the determination of the amount of emanation present gave the most satisfactory results. To get the activity of radium, the emanation liberated by fusing samples of the material to be tested with anhydrous potassium acid sulfate was collected and then measured in an emanation electroscope after the manner described in a later paragraph. The activity of polonium was determined by depositing it on copper,⁵ and then comparing the activity with that of

¹ McCoy and Bunzel, *THIS JOURNAL*, 31, 367 (1909).

² *Phil. Mag.*, 2, 176 (1906).

³ McCoy and Viol, *Ibid.*, 25, 357 (1913); McCoy, *Phys. Rev.*, 1, 401 (1913).

⁴ *Am. J. Sci.*, 25, 269 (1908).

⁵ Marckwald, *Physik. Z.*, 4, 51 (1903); *Ber.*, 2662 (1903).

the standard uranium film. In the case of ionium, where the final residue containing it was very small, the material was dissolved and thin films, satisfactory for α -ray measurement, obtained from the deposit left by evaporating portions of this solution. The activity of the radio-lead and actinium was determined by thin films made in a manner similar for those used for measuring the activity of the original ore, the final measurements being made after the films were a year old.

Since no single method has yet been found that is applicable for treating all carnotites, it was thought desirable in this work to make a study of some of the principal methods already proposed, and to determine, therefore, to what extent these methods must be modified in order to be most effective in the treatment of our ore. Accordingly, the following experiments were made:

(a) **Extraction of Vanadium with Caustic Soda.**—This method is based on the fact that a vanadium ore forms a soluble metavanadate by treating it with a caustic soda solution. Fischer, in a paper on the extraction of vanadiferous sandstone concentrates,¹ states that in his opinion only methods which employ a caustic alkali promise commercial success. In working on crude ore, Fischer found it impossible, by wet methods, even by boiling, to obtain satisfactory results unless he used commercially prohibitive quantities of alkali in which case nearly complete extraction of vanadium was obtained. Excessive consumption of caustic alkali was apparently due to its action on the silica in the ore. With carnotite, however, he was able to get from 87–98% extractions of vanadium with much smaller consumption of alkali, by treating them in the following manner: The concentrates were added to water containing alkali, in the proportion of five parts of concentrates to one part of alkali, and the whole mixed to a pasty consistency and then evaporated to dryness, finishing at a temperature ranging between 200° and 300°. This method, when applied to a *crude* ore, on the contrary, yielded only about a 65% extraction of the vanadium.

The following are the results of my experiments: 100 g. of carnotite were mixed with 50 g. of caustic soda dissolved in 200 cc. of water and boiled for three hours in a flask with a reflux condenser. A sample of the solution then showed about 45% of the vanadium had been extracted. When the mass was boiled for six hours longer, the amount of vanadium extracted had not increased. Thus it was evident that this method could not be used if the vanadium were to be removed completely by a single treatment. Fusion with caustic soda was tried, but not very thoroughly investigated, for it was evident that with such a procedure much difficulty in filtering and washing would be experienced, because

¹ *Met. Chem. Eng.*, 10, 469 (1912).

some of the silica in the ore was converted into sodium silicate which, on acidifying, interfered with subsequent processes.

(b) **Treatment of Carnotite with Carbonate of Soda.**—A method of extracting uranium and vanadium from carnotite with sodium carbonate solutions has been patented by Haynes and Engler.¹ This method, as described by Moore and Kithil,² involves the boiling of the carnotite ore, which has been crushed to twelve mesh with an alkaline carbonate solution until the uranium and vanadium have dissolved. The time of boiling and the strength of solution depend upon the proportion of the two elements present. In the clear filtrate resulting, the uranium is then separated from the vanadium by precipitating the former with sodium hydroxide. This process in actual operation with carnotite is said to give an extraction of 80% of uranium and 60–65% of vanadium.

After some preliminary experiments which seemed to promise good results, the above method, with modifications, was carefully investigated. 100 g. of carnotite were boiled with reflux condenser for three hours with 100 g. of anhydrous carbonate of soda dissolved in 250 cc. of water. After filtering, a sample of the filtrate was neutralized with acid, reduced with zinc and sulfuric acid, and the resulting solution titrated with potassium permanganate. The solution was filtered and the residue treated twice successively in a similar manner with soda solutions, except that the heating in each of these last two cases was continued for only 1½ hours. Analyses of the solutions showed the relative extracts to be approximately as 9 : 2 : 1/3. A test on the third filtrate showed very little uranium present. When these three solutions were combined and concentrated by boiling, a yellow precipitate appeared, which was found on subsequent analysis to be sodium uranyl carbonate. By removing this precipitate and further concentrating the filtrate it was possible, on cooling to low temperatures, to crystallize out a large part of the unused sodium carbonate in a form easy to wash free from impurities. When the insoluble residue from the three consecutive treatments with soda solutions was boiled with hydrochloric acid, the filtrate was green in color and contained large quantities of vanadium. This experiment showed that two treatments with a boiling sodium carbonate solution removed most of the uranium from the ore, giving a solution from which both the uranium and most of the soda could be recovered by simple processes. This method, however, had failed to bring the vanadium completely into solution, a result which is in accord with that found by Haynes and Engler, as cited above.

(c) **Treatment of Carnotite with Carbonate of Soda in the Presence of an Oxidizing Agent.**—Since the treatment of carnotite with soda alone,

¹ U. S. patent 808,839 (1905).

² *Bulletin* 70, Bureau of Mines (1913).

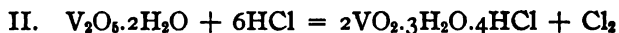
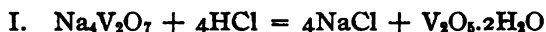
as described in (b), had failed to bring all the vanadium into solution, it was thought that by converting this element into its most highly oxidized form, its extraction might be more complete. In impure carnotites in which the vanadium often occurs both in the trivalent and pentavalent forms, it has been observed that the vanadium dissolves much more readily in alkaline solvents in the latter condition. With these facts in mind, therefore, the following experiment was made:

100 g. of carnotite were boiled with reflux condenser for 41 hours with a concentrated sodium carbonate solution. The heating was continued for so long a time in order to secure maximum extraction by the soda alone. Samples of the solution were examined from day to day, as in (b), but no increase in extraction was noticeable after the boiling had continued 26 hours. During the last six hours of the boiling, a current of chlorine gas was passed into the solution but, on comparing samples of the solution both before and after the introduction of the chlorine gas, no change in the vanadium content was found. In this experiment nearly all of the uranium was found in the soda solution while a considerable part of the vanadium was left in the insoluble residue. These facts show that that part of the vanadium not readily soluble in a soda solution is present in some inert form, probably a silicate such as roscoelite.

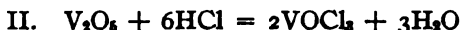
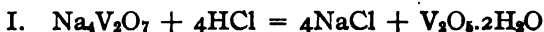
(d) **Treatment of Carnotite with Hydrochloric Acid.**—Among the various methods of treating carnotite is one proposed by Moore and Kithil,¹ which consists in treating the ore directly with concentrated nitric or hydrochloric acid. Pure carnotite dissolves in cold, even dilute acids. In the case of vanadiferous silicates such as roscoelite, Moore and Kithil state that they were able to decompose such ores by boiling them for an hour with the concentrated acids. With the ore used in this work, hydrochloric acid did not seem to bring the vanadium completely into solution, for in an experiment in which 5 g. of the ore were boiled with concentrated acid for intervals of twenty to thirty minutes, ten or twelve successive treatments were required to extract all vanadium. In dealing with kilogram lots, where the ore had been previously treated with sodium carbonate solution, the residue, after three consecutive treatments with concentrated hydrochloric acid diluted with three times its volume of water and boiling for two or three hours, still held vanadium. Although Moore and Kithil are correct in stating that pure carnotite is readily soluble in hydrochloric acid, the facts just stated show that so-called carnotite of the kind here studied, the one which constitutes the bulk of the material available in America for technical processes, is a complex mixture, not all of which is readily attacked even by boiling hydrochloric acid.

¹ *Bulletin 70, Bureau of Mines (1913).*

(e) **Treatment of Carnotite with Dry Hydrogen Chloride.**—It was shown by Smith and Hibbs¹ that sodium pyrovanadate is acted on by dry hydrogen chloride between room temperature and 440° with the formation of common salt and the complete elimination of the vanadium in volatile form. The application of a gentle heat caused a reddish brown vapor to appear which condensed in the combustion tube as an oily liquid easily taken up by water. They explained the reaction, in this case, in the following way:



except that they were not certain that the volatile compound had the composition $2\text{VO}_2 \cdot 3\text{H}_2\text{O} \cdot 4\text{HCl}$. Ephraim,² however, in working on the same problem, showed that the volatile compound of Smith and Hibbs is vanadyl trichloride, VOCl_3 , and has given the following equations in support of his concentration:



In analyzing carnotite, Hillebrand³ has used this method for the separation of vanadium. It was necessary, however, for him to oxidize with nitric acid any vanadium reduced during the process and to repeat, therefore, the treatment with dry hydrochloric acid gas before complete separation could be effected.

To see if this same method would remove the vanadium from our ore, the following experiments were made: 20 g. of carnotite were heated for one or two hours in a retort through which dry hydrogen chloride was passed. Reddish brown fumes of vanadyl trichloride appeared at once and condensed in the neck of the retort, or collected in the water in the receiver. During the process, the retort was frequently shaken so as to insure contact of the gas with all parts of the ore. Seemingly, the method promised success; but analysis of the distillate showed that only about 20% of the vanadium had been removed. On continuing the process for some time longer with increased heating, more of the vanadium passed over, but the distillate, at these higher temperatures, contained considerable ferric chloride. When the involatile residue was washed with water, and the filtrate treated with sodium hydroxide, a heavy precipitate of sodium uranate formed, indicating that during the operation the uranium had been brought into a condition soluble in water. On account of the appearance of the iron in the distillate and the low percentage of vanadium extracted, the process was modified as follows:

¹ THIS JOURNAL, 16, 578 (1894).

² Z. anorg. Chem., 35, 66 (1903).

³ Hillebrand, Am. J. Sci., 10, 120 (1900).

An electric furnace was substituted for the retort in order to be able to control the temperature. 10 g. of the dried ore were placed in a quartz tube into which dry hydrogen chloride gas was passed as the temperature was gradually increased. This tube was frequently rolled to insure uniform heating and mixing, and the process continued for the greater part of a day. In the light of Hillebrand's¹ observations, *i. e.*, that hydrochloric acid reduces a good deal of the vanadium and leaves it in a condition incapable of forming the volatile body, some dry chlorine gas was conducted through the tube during the latter part of the period, in the hope that the vanadium would be kept completely oxidized, and consequently, a complete extraction be obtained. On examining the distillate, however, it was found that ferric chloride had again been carried over, and that not more than about 40% of the vanadium had been removed from the ore, even when the process had been continued throughout the day. On account of the slowness of the reaction and the incompleteness of the extraction, the method was abandoned as an impractical one for treating carnotite on a large scale. It is probable that all the vanadium in the form of true carnotite is volatile, under the conditions of the experiment, incomplete extraction being due, as in other methods, to the presence of vanadium silicates.

(f) **Treatment of Carnotite with Nitric Acid.**—In working on the new American ore, to which they gave the name carnotite, Friedel and Cumenge,² after having extracted the vanadium by using dilute nitric acid, were able to separate the vanadium in the filtrate from other ingredients by evaporating the solution to dryness. Under these conditions, they claim, the vanadium, in excess of nitric acid, becomes insoluble upon evaporation and can be separated quantitatively from uranium whose nitrate is soluble in water. Hillebrand,³ however, in using this method of Friedel and Cumenge on some complex ores, found that he could not always get perfect separation, because it was impossible for him, first, to prevent a little of the vanadium going into solution with the uranium, and, second, to prevent small amounts of the uranium being retained with the vanadium.

In working on our carnotite, it was not possible with dilute nitric acid to get the vanadium completely into solution, as had Friedel and Cumenge. Besides, when the filtrate obtained in this way was concentrated, the insoluble vanadium precipitate which formed carried with it radioactive matter. These results indicate that nitric acid is not a suitable reagent for the primary treatment of carnotite. Naturally there are other reasons why the use of nitric acid would be avoided, if possible, in a technical process.

¹ *Am. J. Sci.*, 10, 120 (1900).

² *Chem. News*, 80, 16 (1899); *Compt. rend.*, 128, 532 (1899).

³ *Am. J. Sci.*, 10, 120 (1900).

(g) **Treatment of Carnotite with Sulfuric Acid.**—A method of treating carnotite, originated by Herman Fleck, which uses dilute sulfuric acid directly on the crushed ore, is said to have been employed practically for extracting uranium and vanadium from carnotite. This method which brings the two elements mentioned into solution leaves the radium in the residue.

With our ore, that part of the vanadium held in the residue left from a carbonate treatment, such as described in (c), could be removed if treated with sulfuric acid. In an experiment on 100 g. of material, this extraction was practically complete, when the residue mixed with 35 cc. of concentrated acid and 115 cc. of water was heated to boiling for $2\frac{1}{2}$ hours. The extraction of vanadium was very complete when the ore, mixed with sulfuric acid and water, was heated until the excess of acid slowly fumed away. This method, nevertheless, even though it did remove uranium and vanadium completely, was not used because of the difficulties it involved in recovering radium with any high degree of efficiency.

(h) **Treatment of Carnotite with an Acid in the Presence of a Reducing Agent.**—In all the acid extractions, except perhaps in some stages in the nitric acid treatment, the filtrate appeared green or blue, depending upon the degree to which the vanadium had been reduced. Acid solutions of vanadium pentoxide are reduced to vanadium dioxide in the presence of sulfurous acid, and by the evaporation with hydrochloric acid. Magnesium with hydrochloric acid reduces the pentoxide to vanadium trioxide, while zinc and hydrochloric acid carry the reduction to vanadium monoxide. Since vanadium, therefore, takes a reduced form in acid solutions, it was thought that the introduction of a reducing agent at the time the acid was acting on the original ore might, perhaps, increase the degree of extraction. Accordingly, 5 g. of ore were placed in each of two flasks containing three cc. of concentrated sulfuric acid diluted with 15 cc. of water. In the one flask were added some pieces of zinc, and the two solutions heated to boiling for some time, under the same conditions; but when the filtrate was examined no increased extraction had occurred from the use of the reducing agent. Similar experiments, using dilute sulfuric acid with and without the addition of sulfur dioxide, showed no difference in the degree of extraction.

As a result of the foregoing experiments, it was evident that this carnotite held part of the vanadium in a condition very difficult to remove by a single operation. In studying some of the Colorado carnotites, Hillebrand¹ had found the vanadium to exist in the ores in two distinct forms: (a) the one, the pentavalent vanadium, quite easily soluble, and (b) the other, a trivalent form, a vanadiferous silicate, extremely difficult to

¹ *Am. J. Sci.*, 10, 120 (1900).

bring into solution. While pure carnotite dissolves at once in cold dilute nitric acid, the vanadiferous silicate yields only to more powerful attacks. The ore used in this work resembled the latter closely in its characteristics, and after the series of preliminary experiments, it was decided that it would be more advantageous not to try to remove the vanadium by a single process, but to treat the ore by methods calculated to recover the radioactive materials, leaving the vanadium to be dealt with wherever it occurred in the various solutions. On the basis of the foregoing work and that described in succeeding pages, the following method was adopted as the most satisfactory: The ore was treated first with a boiling solution of sodium carbonate, then with hydrochloric and nitric acids, respectively, and finally with sulfuric acid. The details of the complete process, with descriptions and discussions of how the different radioactive ingredients were obtained, are given below.

Details of the Method Used in Treating Kilogram Lots of Carnotite.

Since the foregoing experiments seemed to indicate that the treatment of the ore with sodium carbonate solution gave most satisfactory results, this method, therefore, was carefully investigated. Various experiments were made on 100 g. lots to ascertain, first, what concentration of sodium carbonate solution was most effective and, second, what conditions of temperature gave best results. The mass of ore was then increased to a kilogram; and after five or six of these had been worked over, a final kilogram was treated in the following manner:

One kilogram of carnotite and 400 g. of chemically pure anhydrous sodium carbonate were mixed with about two liters of water and heated to boiling for several hours. This mixture was frequently stirred to secure uniform heating, water being added as the mass thickened. While still hot, it was filtered under suction through a filter cloth, and the filter cake washed with hot water. The washing was a slow process, but attempts in preceding experiments on boiling up the residue with water had proved that it made the mass more colloidal and, consequently, more difficult to filter. Decantation processes were also abandoned because of the slowness with which the mud-like material settled. The brown filtrate thus obtained contained most of the uranium, less than half of the vanadium, and the unchanged portion of the sodium carbonate. After attempts to separate the uranium from the carbonate solution by means of a variety of reactions, a very simple and effective method was finally discovered. It was found that when the carbonate solution was evaporated so that the solution became nearly saturated with sodium carbonate, the uranium settled out as a beautiful, yellow product easily filtered from the hot solution. This substance which on analysis proved to be uranyl sodium carbonate, $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$, was quite heavy, and settled quickly. To obtain the maximum recovery of this compound, the evaporation was

continued up to the point at which the sodium carbonate just began to crystallize out, and the hot solution was filtered at once. Strong suction left the uranyl sodium carbonate almost free from impurities, so that very little, if any, water was required in washing to give a relatively pure product. The amount of dry precipitate obtained in this way from each kilogram of carnotite concentrate varied from 85 to 90 g. In this final kilogram lot, the weight of the uranyl sodium carbonate was 88.1 g.; this was 88% of the total amount of uranium in the ore. An examination of the filtrate from the uranyl sodium carbonate precipitate showed it still contained 2% of the uranium. When the residue from the first carbonate extraction was treated again with 300 g. of sodium carbonate under conditions similar to the above, the amount of uranium carried in this filtrate was too small to be recovered as uranyl sodium carbonate. On examining the filtrate, however, the uranium found was only 2.8% of the total amount in the ore. It thus appears that a second treatment with sodium carbonate solution is an unnecessary step in the operation.

The identity of the yellow compound referred to in the preceding paragraph was established by analysis. Some of the material was heated at 125° to constant weight. The loss, which amounted to about 1%, was due undoubtedly to moisture held mechanically. The residue of silica, etc., left on dissolving some of the compound in dilute sulfuric acid, amounted to about 0.3%. The determination of the uranium was made by reducing a weighed amount of the yellow body with zinc and sulfuric acid, and then titrating with potassium permanganate. Sodium was determined by removing the uranium with ammonium hydroxide, and then converting the sodium compound into the sulfate. This analysis, as indicated by the figures below, proved the compound to be uranyl sodium carbonate.

RESULTS OF ANALYSIS.

COMPOSITION OF THE PORTION FREE FROM
VOLATILE AND INSOLUBLE MATTER.

	Per cent.		Found.	Calculated for $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$
Loss on heating at 125°.....	0.98	Uranium.....	43.65	43.97
Insoluble residue.....	0.31	Sodium.....	17.07	16.96

The uranyl sodium carbonate obtained by the same method on other kilogram lots, had been carefully examined to see if any of the other radioactive substances had been carried along with the uranium. Portions of the compound were dissolved and attempts made to find polonium, radium, ionium and actinium by methods described in later paragraphs of this paper, but in none of these experiments was there found any active substance other than uranium. The solution filtered from the uranium carbonate contained a large excess of unchanged soda together with the sodium vanadate. This solution was evaporated until it became saturated with the soda, and then cooled to 0°. Sodium carbonate is more than

six times as soluble at 100° as at 0° , so that large masses of crystals were obtained when the boiling saturated solution was cooled. With a little ice water these crystals could be washed nearly free from the vanadium which remained in solution. By further evaporation, other crops of crystals could be obtained, and in this way most of the uncombined soda recovered. The sodium carbonate thus obtained could be used repeatedly in treating the original ore and thereby a great saving of that compound be realized. As vanadium can be obtained from its solutions by well-known methods, the sodium vanadate solution left after the removal of the uranium and the excess of sodium carbonate, was studied only in so far as to find that none of the radioactive elements were present in it.

After the original ore had been treated with a solution of carbonate of soda, the next step was to boil the residue with hydrochloric acid. In preceding experiments it had been found that, if dilute acid were used only in such quantities as to break up the easily decomposed carbonates and not in sufficient amounts to bring into solution any of the iron or vanadium, the yield of radium was not more than 60-65% of the total amount in the ore. By boiling with more concentrated acid, the percentage of radium recovered could be greatly increased. Further, three consecutive treatments with boiling hydrochloric acid, made by mixing one volume of concentrated acid with about three volumes of water, still left radium in the residue, most of which could be removed by boiling the residue with nitric acid diluted with three or four times its volume of water. Consequently, a single treatment with hydrochloric acid, followed by one with nitric acid, was found to be the most satisfactory method to follow. In accordance with these results, the residue left from the carbonate treatment of the last kilogram of ore was boiled with 400 cc. of concentrated hydrochloric acid diluted with two or three times its volume of water. The heating was continued for about eight hours, water being added as it disappeared by evaporation. The hot mixture was then filtered and the filtrate evaporated to a smaller bulk. This solution was then carefully examined for radioactive elements. Fifty cc. of a 1% bismuth nitrate solution were added and completely precipitated with hydrogen sulfide, the excess of which was removed from the filtrate by boiling it, after the sulfides had been collected on a filter. These sulfides were then dissolved in concentrated nitric acid, sulfuric acid was added to the solution, and the lead was separated from bismuth by the customary analytical methods. The lead sulfate removed in this way contained the radio-lead. The bismuth in the filtrate was precipitated with ammonium hydroxide, and after filtering and washing it was dissolved in hydrochloric acid. It was in this solution that most of the polonium appeared. To the filtrate from the sulfides, 3 or 4 cc. of concentrated sulfuric acid were added which caused the precipitation of radium and

barium as sulfates. Small amounts of barium chloride were now added, and a second and third precipitation was made for the purpose of carrying down the radium and actinium more completely, especially the latter. The filtrate from barium sulfate was then neutralized with ammonia up to the point of precipitation of the hydroxides, 5-10 g. of cerium chloride or nitrate were added, and the cerium was precipitated with oxalic acid. This was a troublesome process, as it necessitated the use of large amounts of oxalic acid before precipitation of cerium oxalate could be brought about. The activity of the cerium oxalate, precipitated in this way, was much too little to account for all the ionium and it was the lack of radioactivity at this point which led to the belief that the ionium had not yet been removed from the residue. When some thorium nitrate was added to this filtrate, instead of cerium, and a precipitation of thorium oxalate was made with oxalic acid, no better recovery of ionium was obtained.

The residue from the hydrochloric acid extraction was next treated with 200 cc. of concentrated nitric acid diluted with about a liter of water. This was kept at boiling temperature for a day, at the end of which time the mass was filtered. The resulting filtrate was examined for radioactive elements by methods similar to those used in studying the hydrochloric acid filtrate, but none of these elements could be found except radium. On the addition of a few cc. of sulfuric acid to the filtrate, a precipitate formed which showed the presence of considerable activity. In short, nitric acid always brought into solution soluble matter containing radium, which hydrochloric acid was incapable of dissolving out of the ore.

The final step in the process was that which involved the use of sulfuric acid. The residue left from the foregoing extractions was mixed with twice its weight of sulfuric acid which had been diluted with water in the proportions of about five of acid to four of water. This was slowly heated and the temperature so regulated that most of the acid fumed away. If the heating was not excessive, on digesting the resulting mass with hot water, the residue was pure white, for all vanadium and iron remaining in the ore were completely removed by this process. It was in this filtrate that most of the ionium was found. To remove it, about 10 g. of cerium nitrate were added, and the excess of sulfuric acid was neutralized with ammonium up to the formation of a small amount of the hydroxides. A large quantity of oxalic acid was then added, which dissolved the slight hydroxide precipitate, and after some time precipitated the cerium as oxalate. This process was difficult to carry out, for it seemed impossible to precipitate the cerium oxalate until the solution was almost saturated with oxalic acid. Keeping the solution well stirred and rubbing the sides of the containing vessel with a glass rod aided considerably in the pre-

nitration. In order to recover the ionium more completely, a second portion of cerium nitrate was added to the solution and a second precipitation of cerium oxalate was obtained. The methods used in concentrating the ionium and in measuring its activity are given later in the special paragraph on ionium.

Radium.

The complete method of treating the ore, as described in preceding paragraphs, gave a good recovery of radium, the greater part of which appeared in the solution obtained from the hydrochloric acid extraction. To get the best results it was necessary, however, to follow the hydrochloric acid treatment with a nitric acid extraction because the latter dissolves material insoluble in hydrochloric acid, which still contained about 8-10% of the radium. In working up the last kilogram of ore, the barium radium sulfate precipitate obtained from the hydrochloric acid filtrate weighed 7.36 g. and that from the nitric acid solution 0.45 g. On the addition of successive small equivalent amounts of barium chloride and sulfuric acid, 9.30 g. of barium sulfate were precipitated in the filtrates and the first precipitates of this substance.

The percentage of recovery of radium was determined by comparing the activity of the original ore with that of the radium barium sulfate, the emanation method being used for the purpose. To do this, one-half gram of the original ore, after being mixed with 5 or 6 g. of anhydrous potassium acid sulfate, was carefully fused in a hard glass test-tube and made air tight. After several days this mass was again fused, the emanation transferred completely to an emanation electroscope (without use of water), and the time of discharge observed. By knowing the half interval the tube was sealed, the time of discharge for the maximum amount of emanation could be calculated from the known rate of decay and half of radium emanation. In a similar way, the activity of the radium barium sulfate was obtained, except that in this determination only 0.0150 g. of material was used in each fusion. On comparing these results, it was found that 89.9% of the total radium had been recovered in the barium radium sulfate precipitated from the hydrochloric and nitric acid solutions. The barium sulfate obtained by adding small amounts of barium chloride to the filtrates, as described above, was only slightly active and contained but 2.7% of the radium. The residue left after all extraction processes contained only 4.2% of the total radium contained in the ore. It leaves 3.3% of the radium unaccounted for.

Polonium and Radio-lead.

The filtrates from the first three treatments of the ore, *i. e.*, with carbonate of soda, with hydrochloric acid and with nitric acid, were examined for polonium and radio-lead, which were found only in the chloride filtrate. When the filtrate from the carbonate extraction was examined

for polonium by adding to it a little bismuth nitrate and then precipitating with hydrogen sulfide, no polonium was found in the bismuth sulfide. The sulfides, obtained by treating the hydrochloric acid filtrate in a similar manner, were comparatively active. These sulfides were dissolved in boiling concentrated nitric acid, sulfuric acid was added to the solution, and the lead was separated from the bismuth by the usual analytical methods. It was not necessary in any of these experiments to add any lead salt to carry down the radio-lead, since the original ore contained small quantities of that element. The lead sulfate which was only slightly active at first, greatly increased in radioactivity in the course of ten months. The bismuth and polonium, after being separated from the lead, were further purified by precipitating them with ammonium hydroxide. This precipitate was then filtered out and, after being dissolved in a few drops of hydrochloric acid, the solution was examined quantitatively for polonium by depositing it on copper. In the last kilogram lot the bismuth chloride obtained, as described above, was diluted with water up to 250 cc., enough hydrochloric acid being added to keep the bismuth in solution. Five cc. samples of this solution were further diluted with about the same volume of water and introduced into a beaker containing a clean piece of copper foil, the under side of which had been covered with wax. Under these conditions, the polonium deposited on the copper, the process being hastened by stirring with a current of air, so that in 30 or 40 minutes a large part of the polonium had collected on the copper foil. In an experiment which had run 30 minutes, the first foil was removed and a second and a third were introduced into the same solution, for about the same length of time. The activity of the polonium deposited on these three foils varied as 11 : 2 : 1/6, showing that more than 80% of the polonium, in the 5 cc. sample, had deposited on the first copper foil in 30 minutes. When the total polonium activity was calculated, it was found that about 50% of the amount in the original ore had been recovered in the filtrate from the hydrochloric acid extraction. When the nitric acid solution was treated in the same way as the hydrochloric acid filtrate, the bismuth sulfide obtained did not contain any polonium.

Ionium.

In this research, great effort was made to discover what course the ionium took and how it could be recovered to best advantage. The filtrate from each of the first three extractions, *i. e.*, with soda, with hydrochloric acid, and with nitric acid—was therefore carefully examined. As this ore contained only small quantities of the rare earths, a little thorium or cerium salt had to be introduced into the filtrate in order to get a precipitate on the addition of oxalic acid. The oxalates thus obtained should have carried down whatever ionium there was in the filtrate. When the solution from the sodium carbonate extraction was examined

in this way, no ionium was found. Likewise the filtrates from the hydrochloric and nitric acid extractions showed but very little more activity than could be accounted for by the thorium added. From these results it was evident that the ionium had either escaped detection or had not yet been removed from the insoluble siliceous residue. An examination of the latter, by means of the emanation method, showed that approximately 95% of the radium had already been removed from the original ore. But the α -ray activity of the residue, as measured by thin films, was considerably greater than could be accredited to the 5% of radium left therein. In order to remove this radioactive substance, the residue was finally treated with sulfuric acid, as already described, because it was believed that if any radioactive matter were dissolved by this acid, it would not be radium, but might be ionium. Further, it was thought that the rare earths might be present in some form like the fluorides and that drastic treatment such as boiling with concentrated sulfuric acid would be required to remove them. This method proved successful, for, when this mass was digested with boiling water, the filtrate not only contained all the vanadium left in the residue, but also the greater part of the ionium. When a small amount of thorium nitrate was added to the filtrate, thus obtained, and the thorium precipitated as oxalate, it always possessed much greater activity than had been observed in the filtrates from any of the other extractions. The ore did not contain enough, if any, thorium to carry down the ionium without the addition of thorium. But as thorium and ionium cannot be separated by any known reaction and as we wished finally to obtain ionium mixed with a minimum of thorium, cerium was added to the sulfate solution instead. It was found difficult, however, to precipitate cerium oxalate in acid solution in the presence of vanadium and iron, but it could be accomplished by almost neutralizing the sulfuric acid with ammonium hydroxide and then adding oxalic acid until it had nearly saturated the solution. To get the ionium in a more concentrated condition, the resulting cerium oxalate was thoroughly shaken with a solution made by dissolving 40 g. of dry sodium carbonate and 20 g. of sodium bicarbonate in 400 cc. of water, 10 cc. of which were used for each gram of cerium oxalate. Under these conditions a large portion of the ionium was dissolved while the cerium remained behind as an insoluble carbonate. When the cerium carbonate thus obtained was dissolved in nitric acid, the solution neutralized with ammonia, and then hydrogen peroxide added, upon heating to 70° the balance of the thorium and ionium were precipitated. The residue carrying the ionium was very small; it probably consisted essentially of thorium, which may have been contained originally as an impurity in the cerium used. A test made on some of this material by means of the emanation method showed not the slightest trace of radium and films

made from these ionium residues remained constant in activity for ten months. When the ionium was separated from the last kilogram of ore in the manner just described and its activity measured by the method given in a preceding paragraph, the results showed the recovery for this element to be about 61% of the total amount calculated for the original ore.

Actinium.

Just as in the case of the other radioactive elements, the filtrates obtained from treating the ore in succession with carbonate of soda, with hydrochloric acid, and with nitric acid, were examined for actinium. As actinium is said to occur with ionium in the rare earth precipitates, all the precipitates of cerium and thorium oxalates made in studying ionium were likewise examined for actinium, but there was no evidence to show that the actinium accompanied the ionium in the course the latter took before being recovered from this ore. Actinium, however, was found to be carried down with the barium sulfate containing the radium. That it might be the more completely recovered, small amounts of barium chloride were added and several precipitations of the barium sulfate made in the filtrates from the hydrochloric and nitric acid extractions. These combined sulfates were then fused with a mixture of sodium and potassium carbonate in molecular proportions, the barium carbonate was thoroughly washed, and then converted into chloride. On adding ammonium hydroxide to this solution, a precipitate formed which, although but slightly active at first, grew in activity until the increase amounted to fifteen- or twenty-fold, the rate of increase being about that expected for actinium initially free from radioactinium and actinium X. The actinium, moreover, was not all removed from the barium in this way for, by adding 1 or 2 g. of an aluminium salt to the radium barium solution and then precipitating the aluminium with ammonium hydroxide, a precipitate was obtained which also increased many-fold in activity. To prevent any radium from being held by the aluminium hydroxide, the latter was dissolved and reprecipitated three times and the activity of the actinium under these conditions was then measured. In the experiments on the last kilogram of ore, 2 g. of aluminium nitrate were added to the barium solution and precipitated in the manner described above. The aluminium hydroxide thus obtained increased in activity about thirty-five-fold in twenty-five days. A second precipitation using the same amount of aluminium nitrate gave a precipitate which, while not so active at first as the former one, increased more than seventy-five-fold in the same interval of time. From these results it is clear that the actinium contained in the barium radium solution cannot be separated completely by a single precipitation of aluminium hydroxide in this solution. The percentage of actinium found by the above treatment, was 52% of the total amount as calculated in a preceding paragraph.

Summary.

In this paper a careful study has been made of a Colorado carnotite and a satisfactory method worked out for the extraction of the radioactive ingredients. Several of the commercial methods now in use for removing vanadium and uranium from a carnotite ore have been examined and modified so as to be effective in treating our ore which was found not to be a pure carnotite, but a mixture of this mineral with a vanadiferous silicate, containing the vanadium in a condition difficult to remove. The method finally adopted gives good results. The uranium is removed by boiling the carnotite concentrates with a sodium carbonate solution, precipitated as uranyl sodium carbonate by merely concentrating the filtrate, and the soda is again recovered. The radium, actinium and radio-lead are contained in the filtrate obtained by boiling the residue insoluble in soda solution with hydrochloric acid. That part of the radium still held in the residue is then removed with boiling nitric acid. The ionium is finally recovered from the residue by boiling with sulfuric acid and is then concentrated with cerium rather than with thorium, from which it cannot be separated by any known reaction. A summary of the processes used and the results obtained from the last kilogram of carnotite concentrates is here given.

One kilogram of carnotite concentrates was boiled for several hours with 2 liters of a solution containing 400 g. of anhydrous sodium carbonate. The filtrate yielded 88.1 g. of uranyl sodium carbonate, $\text{UO}_2\text{CO}_3 \cdot 2\text{Na}_2\text{CO}_3$, which represented 88% of the total uranium in the sample. The filtrate still held 2% of the uranium in solution. A second treatment of the ore with 300 g. of sodium carbonate, under the same conditions as above, dissolved out only 2.8% of the uranium. The residue was treated with 400 cc. hydrochloric acid diluted with about a liter of water, and boiled eight hours. The barium radium sulfate separated from the filtrate weighed 7.36 g. The residue was next heated a day with 200 cc. of nitric acid diluted with about a liter of water. The barium radium sulfate precipitated in this filtrate weighed 0.453 g. The percentage of radium in these combined sulfates was 89.8% of the total amount in the ore. Reprecipitations of barium sulfate in the two acid filtrates carried down 2.7% more of the radium. The lead sulfate, separated from bismuth and containing the radio-lead, weighed 0.49 g. The polonium precipitated with bismuth and then deposited on copper was 50.1% of the total amount in the ore as calculated from the ranges of the radioactive elements. The residue was finally treated with twice its weight of sulfuric acid after being diluted with about an equal weight of water, and then heated until most of the sulfuric acid had escaped in fumes. The activity of the ionium found in this solution was 61% of the total amount in the original carnotite, as calculated in a preceding paragraph. The residue left after all ex-

traction processes weighed 507 g., 50.7% of the original ore used. Its activity as measured by the emanation method showed that only 4.2% of the radium still remained in the residue.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

BINARY AND TERNARY SYSTEMS OF THE NITRATES OF THE ALKALI AND ALKALINE EARTH METALS.

By WILLIAM D. HARKINS AND GEORGE L. CLARK.

Received May 25, 1915.

In view of the fact that very few complete ternary systems of mixtures of dry salts have been worked out,¹ the following investigations of new systems were made: (1) a study of the complete system comprising barium, sodium, and potassium nitrates; (2) a study of the eutectic and all neighboring points of the system, strontium, sodium, and potassium nitrates; and (3) a study of the system barium, lithium and potassium nitrates as far as the point beyond which marked decomposition prohibited further determinations. The work of Menzies and Dutt on the system calcium, sodium, and potassium nitrates has been utilized for comparison with these systems by means of the respective triangular diagrams.²

Method of Procedure.

The freezing points of the various salt mixtures were determined by the usual method. Weighed amounts of the dried salts in the calculated proportion were carefully ground together and then melted with the thermometer bulb immersed. As soon as the melts were perfectly clear, the temperature was lowered at the rate of two degrees per minute, and at the same time the temperature was kept constant through the mixture by constant stirring. Upon the appearance of the first minute crystal, the temperature was carefully noted. Such a method permitted several repetitions so as to obtain a good check on the primary results.

Preparation of the Salts.

The salts used were Kahlbaum's "Zur Analyze" preparations, with the exception of the lithium nitrate which was made by J. T. Baker. Preliminary examinations of the purity of the salts made it clear that nothing was to be gained by recrystallization, except that it was found necessary to recrystallize the lithium nitrate from nitric acid solution because the original salt gave a basic reaction with rosolic acid.

¹ The following are the ternary systems which have been completely investigated: The system $\text{Ca}(\text{NO}_3)_2$, KNO_3 and NaNO_3 by Menzies and Dutt, *THIS JOURNAL*, **31**, 1366 (1909). The system LiNO_3 , KNO_3 and NaNO_3 by Carveth, *J. Phys. Chem.*, **2**, 206 (1898). The system Al_2O_3 , SiO_2 and CaO in the Geophysical Laboratory, Washington, D. C., by Rankin and Wright, *Am. J. Sci.*, **39**, 1-79 (1915).

² Roozeboom, *Z. physik. Chem.*, **15**, 143 (1894); Bancroft, *J. Phys. Chem.*, **24**, 441.

In this work it was essential that the salt should be carefully dried. A test of the effect of the presence of water upon the melting point of pure sodium nitrate showed that 0.231 g. of water produced a lowering¹ of 0.8° when present in 40 g. of perfectly dried salt. All of the salts were finely ground and dried in an electric oven through which a constant stream of pure, dry air was passed. The air was conducted through three wash-bottles of sulfuric acid, a soda lime tube, through absorbent cotton, and finally through a long tube containing a mixture of P_2O_5 and glass beads.

Barium, potassium, and sodium nitrates presented no difficulties and were dried at 140°. In the cases of the strontium and lithium salts, however, gentle desiccation was first necessary before the final heating. From 24-48 hrs., drying was necessary to obtain a sufficiently dry salt.

The components of the mixtures to be examined were weighed out to a thousandth of a gram and then intimately ground together. In the cases where lithium or strontium nitrates were present, this process was carried out in an air-tight box in which calcium chloride and sulfuric acid were used for drying, and in the side of this box were two openings into which two rubber gloves were tightly fitted.

The Apparatus Used.

The heating bath used was similar to that used by Menzies and Dutt, but with some added refinements. A thick, hollow cylinder of concrete formed the base upon which a porcelain tower could rest. It was arranged in this way so that the flame of the Meker burner on the inside could be used at its most effective point. Resting on top of the tower and supported upon it by wire gauze was an iron cylinder, five inches high and three inches in diameter, in which was fitted a small circular shelf of asbestos board, as the base for the support of an ordinary lamp chimney. The test-tubes containing the salts were supported inside this by means of an asbestos rack with close-fitting holes. For the mixtures melting below 300° ordinary soft glass tubes, 1.5 × 16 cm., were used, except when lithium nitrate was used. Owing to its etching effect upon sodium glass, hard glass tubes of the same size were substituted. For the higher temperature measurements, Jena test-tubes, 1.75 × 20 cm., were used and found satisfactory even at 600° when not in direct contact with the flame. A correspondingly large amount of salt was taken in these larger tubes.

In order to give uniform heating from the sides rather than from the bottom, a shield was placed between the flame and the test-tube. This

¹ The lowering calculated by the van't Hoff equation $\left(\Delta t_{f.p.} = \frac{RT_{f.p.}^2}{L_f} \frac{N_1}{N_1 + N_2}\right)$

is less than this experimental value if 3690 calories are taken as the value for the latent heat of fusion as given by Goodwin and Kalmus, *Phys. Rev.*, 28, 1 (1908).

consisted of a raised clay triangle covered with iron, which also rested on the asbestos shelf inside the lamp chimney. The stirring rod was circular at the bottom so as to loosely circle the thermometer. For temperatures above 500° , insulation with asbestos paper inside and outside the chimney was found advisable, leaving only space enough to observe the formation of crystals.

Methods of Temperature Measurement.

For temperatures below 250° , a small Gerhardt mercury thermometer was employed, and for those from 250 – 350° a nitrogen-filled mercury thermometer. These were calibrated, immersed always to the same respective levels, against a platinum resistance thermometer of quartz with gold leads for every 5° , in a mechanically stirred crisco bath. This was done several times and the corrections applied. Some measurements were repeated, using the resistance thermometer itself and a good check thus established. For temperatures much above 350° , the nitrogen-filled thermometer proved unsatisfactory in spite of efforts to keep it in close calibration, so a resistance thermometer was used for all temperatures above 350° . In order to protect the fragile platinum coil from the action of the nitrates, the end was covered with a case of platinum foil, brazed with gold. The resistance was determined by a galvanometer and a Wolff box-bridge, which was kept at a temperature of approximately 20° . Corrections were made for the resistance of the copper leads and the temperature determined by means of the Callendar difference formula. Nothing was to be desired in the accuracy of the thermometer in every measurement taken with it. Consequently 595.53° should constitute a value for the freezing point of barium nitrate very close to the true one.

(1) The System Barium, Sodium and Potassium Nitrates.

Eighty-one mixtures corresponding to the points on the triangle shown on Fig. 1 were examined in this system. The three corners represent each of the pure components, the three sides, the three binary systems, and all points within the triangle belong to the ternary system. The sum of the percentages, which are all equivalent rather than weight, is always 100. Points on the intersections, 1 to 66, have percentages of 10 and its multiples, while points 67 to 81 all lie below a barium nitrate concentration of 10% and surround the eutectic (No. 75). Such a triangle, consequently, shows at a glance exactly the composition of all mixtures studied.

For the temperatures below 350° about 20 g. of salt were used, and for the larger test-tubes and longer bulb of the resistance thermometer above 350° , about 30 g. Table I shows the freezing point corresponding to each point represented on the triangle with the equivalent percentages and the actual weights of each of the components.

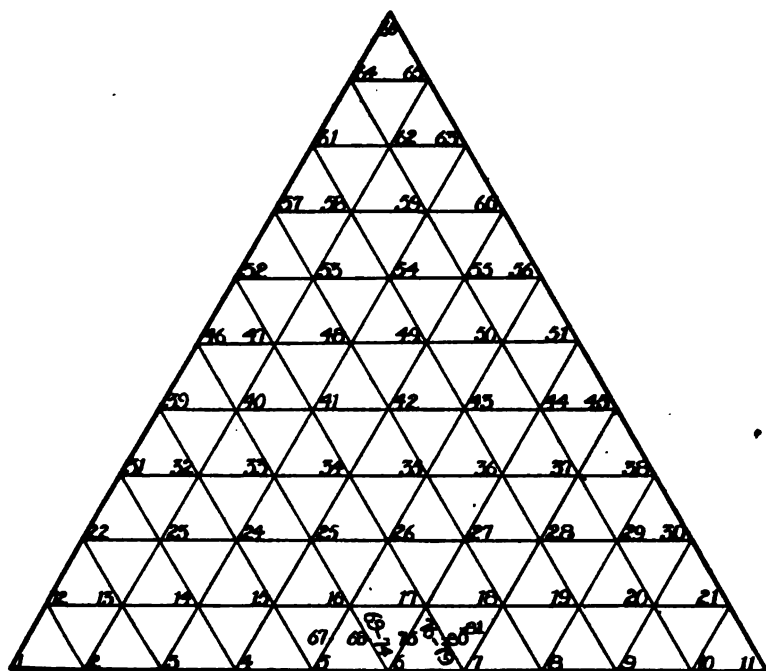


Figure 1

TABLE I.

No.	Eq. % NaNO ₃	Eq. % KNO ₃	Eq. % Ba(NO ₃) ₂	Wt. of NaNO ₃	Wt. of KNO ₃	Wt. of Ba(NO ₃) ₂	Freezing point.
1.....	100	0	0	20	0	0	314.1
2.....	90	10	0	18	2.38	0	290.9
3.....	80	20	0	16	4.76	0	274.1
4.....	70	30	0	14	7.14	0	253.8
5.....	60	40	0	12	9.51	0	235.2
6.....	50	50	0	10	11.89	0	222.4
7.....	40	60	0	8	14.27	0	233.8
8.....	30	70	0	6	16.63	0	257.5
9.....	20	80	0	4	19.01	0	287.3
10.....	10	90	0	2	21.39	0	313.7
11.....	0	100	0	0	23.78	0	346.3
12.....	90	0	10	27	0	4.60	296.6
13.....	80	10	10	16	2.38	3.07	285.0
14.....	70	20	10	14	4.76	3.07	273.9
15.....	60	30	10	12	7.14	3.07	269.4
16.....	50	40	10	10	9.51	3.07	257.5
17.....	40	50	10	8	11.89	3.07	244.9
18.....	30	60	10	6	14.27	3.07	235.2
19.....	20	70	10	4	16.63	3.07	260.0
20.....	10	80	10	2	19.01	3.07	288.1

TABLE I (continued).

No.	Eq. % NaNO ₃ .	Eq. % KNO ₃ .	Eq. % Ba(NO ₃) ₂ .	Wt. of NaNO ₃ .	Wt. of KNO ₃ .	Wt. of Ba(NO ₃) ₂ .	Freezing point.
21.....	0	90	10	0	21.39	3.07	333.8
22.....	80	0	20	24	0	9.20	358.3
23.....	70	10	20	14	2.38	6.14	341.3
24.....	60	20	20	12	4.76	6.14	334.9
25.....	50	30	20	10	7.14	6.14	327.2
26.....	40	40	20	8	9.51	6.14	319.8
27.....	30	50	20	6	11.89	6.14	310.7
28.....	20	60	20	4	14.27	6.14	300.9
29.....	10	70	20	2	16.63	6.14	290.9
30.....	0	80	20	0	19.01	6.14	311.9
31.....	70	0	30	21	0	13.80	396.51
32.....	60	10	30	12	2.38	9.21	384.1
33.....	50	20	30	10	4.76	9.21	380.1
34.....	40	30	30	8	7.14	9.21	371.2
35.....	30	40	30	6	9.51	9.21	364.9
36.....	20	50	30	4	11.89	9.21	353.3
37.....	10	60	30	2	14.27	9.21	345.8
38.....	0	70	30	0	16.63	9.21	350.0
39.....	60	0	40	18	0	18.40	435.31
40.....	50	10	40	15	3.57	18.40	429.44
41.....	40	20	40	12	7.14	18.40	424.72
42.....	30	30	40	9	10.71	18.40	422.85
43.....	20	40	40	6	14.28	18.40	410.61
44.....	10	50	40	3	17.85	18.40	390.20
45.....	0	60	40	0	14.27	12.28	380.08
46.....	50	0	50	15	0	23.00	462.98
47.....	40	10	50	12	3.57	23.00	431.88
48.....	30	20	50	9	7.14	23.00	453.72
49.....	20	30	50	6	10.71	23.00	448.67
50.....	10	40	50	3	14.28	23.00	441.87
51.....	0	50	50	0	11.89	15.35	433.95
52.....	40	0	60	12	0	27.60	484.20
53.....	30	10	60	9	3.57	27.60	483.02
54.....	20	20	60	6	7.14	27.60	484.20
55.....	10	30	60	3	10.71	27.60	476.40
56.....	0	40	60	0	9.51	18.42	474.31
57.....	30	0	70	9	0	32.20	492.64
58.....	20	10	70	6	3.57	32.20	489.21
59.....	10	20	70	3	7.14	32.20	492.04
60.....	0	30	70	0	10.71	32.20	493.87
61.....	20	0	80	6	0	36.80	501.69
62.....	10	10	80	3	3.57	36.80	494.18
63.....	0	20	80	0	7.14	36.80	495.32
64.....	10	0	90	3	0	41.40	529.65
65.....	0	10	90	0	3.57	41.40	514.42
66.....	0	0	100	0	0	46.05	595.53
67.....	55	40	5	11	9.51	1.53	225.2
68.....	50	45	5	10	10.70	1.53	217.1
69.....	49	46	5	9.8	10.94	1.53	216.5

TABLE I (concluded).

No.	Eq. % NaNO ₃	Eq. % KNO ₃	Eq. % Ba(NO ₃) ₂	Wt. of NaNO ₃	Wt. of KNO ₃	Wt. of Ba(NO ₃) ₂	Freezing point.
70.....	48	47	5	9.6	11.18	1.53	216.0
71.....	48	48	4	9.6	11.41	1.23	217.2
72.....	47	48	5	9.4	11.41	1.53	215.5
73.....	46	49	5	9.2	11.65	1.53	214.9
74.....	45	49	6	9	11.65	1.84	217.8
75.....	45	50	5	9	11.89	1.53	214.1
76.....	46	50	4	9.2	11.89	1.23	218.4
77.....	45	51	4	9	12.13	1.23	220.4
78.....	44	53	3	8.8	12.60	0.92	225.5
79.....	44	51	5	8.8	12.13	1.53	215.5
80.....	40	55	5	8	13.08	1.53	217.9
81.....	35	60	5	7	14.27	1.53	229.0

Decomposition was not apparent in any of the melts until a barium nitrate concentration of 80% was reached. In these cases a slight evolution of oxygen began, if the salt was heated too far above the freezing point. By working rapidly, however, and by careful heating, any error produced by the formation of nitrites was reduced to a minimum. When heated for some time these mixtures became yellow in color, showing that even the nitrites break down with sustained heat.¹

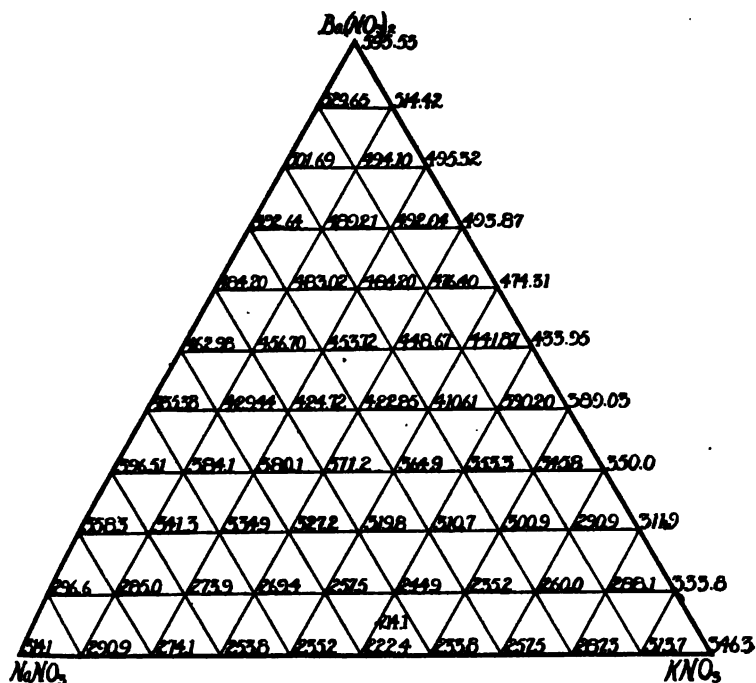


Figure 2

¹ J. Lang, *Pogg. Ann.*, 118, 282.

As each melting point was determined, it was noted down on a triangular figure upon the point of its corresponding percentage composition. Such an arrangement is shown in Fig. 2. The temperatures for all points are recorded, except for numbers 67 to 74 and 76 to 80, all of which are in the neighborhood of the eutectic. In this figure the temperature is variable in the plane perpendicular to the surface of the page and should it actually be represented, a solid figure would result whose upper surface with its highest point at 595.53° and lowest at 214.1° would represent

the true elevation of all temperatures.

Such a condition is represented on a single plane, of course, by isothermal lines. In order to make the relation of these lines simpler, vertical sections were plotted as in Figs. 3, 4, and 5. In Fig. 3 the curves, drawn directly from the triangle, show in series points 1 to 11, 12 to 21, 22 to 30, 31 to 38, 39 to 45, and 46 to 51 with a fixed percentage of barium nitrate in each case.

Similarly, Figs. 4 and 5 show the sections

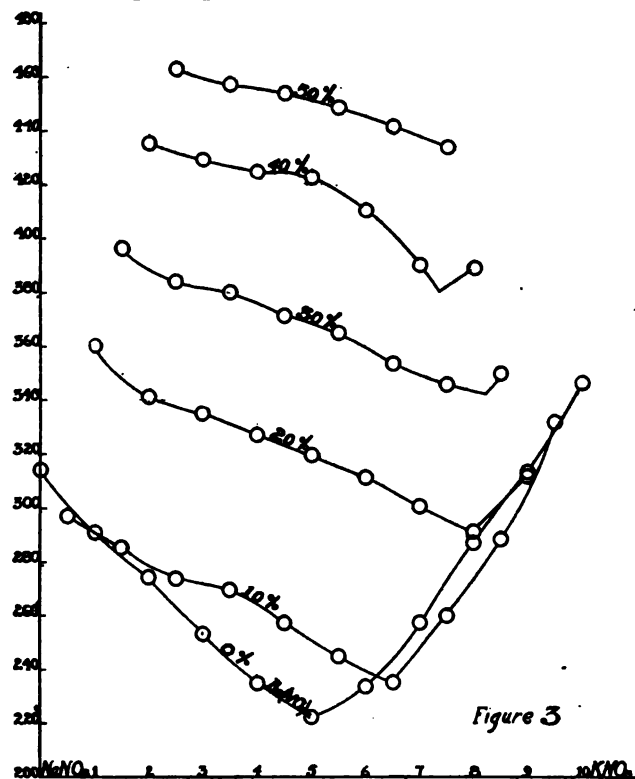


Figure 3

tions from the basis of the other two sides of the triangle along the lines parallel to those sides. Simple measurements upon these curves make it possible to find the equivalent percentages corresponding to temperatures in round numbers at intervals of 10° , and above 500° , of 50° . Points corresponding to the same temperatures are connected by a smooth line, and the complete liquidus surface contour diagram results which is shown in Fig. 6.

As has already been intimated, the work of others has been repeated in some cases. The melting points of sodium and potassium nitrates and points on the binary curve of the two have been determined many

times.¹ The results of Menzies and Dutt were found to be in good accord with the new results, although 314.1° as a value for the freezing point of sodium nitrate, as determined by the writers, is a degree lower than obtained by them, and likewise a difference of 5.7° for a mixture of 50 equivalents each of NaNO_3 and KNO_3 is found. The lower part of the curve obtained by the writers is in better agreement with the measurements of Carveth.²

For the melting point of barium nitrate, 593° was found by Carnelley³ and by Le Chatelier,⁴ in both cases indirectly. By direct measurement the writers found 595.53° . No record of work upon any ternary mixture of barium, potassium and sodium salts could be discovered. Maumené⁵ found a lack of decomposition in mixtures of equal amounts of KNO_3 and $\text{Ba}(\text{NO}_3)_2$ and of NaNO_3 and $\text{Ba}(\text{NO}_3)_2$. The eutectic of the former was determined by Guthrie⁶ to be 278.5° with 29.53% of $\text{Ba}(\text{NO}_3)_2$ by weight. Although not determined exactly in this work, the curve would show a value approximately 15° higher.

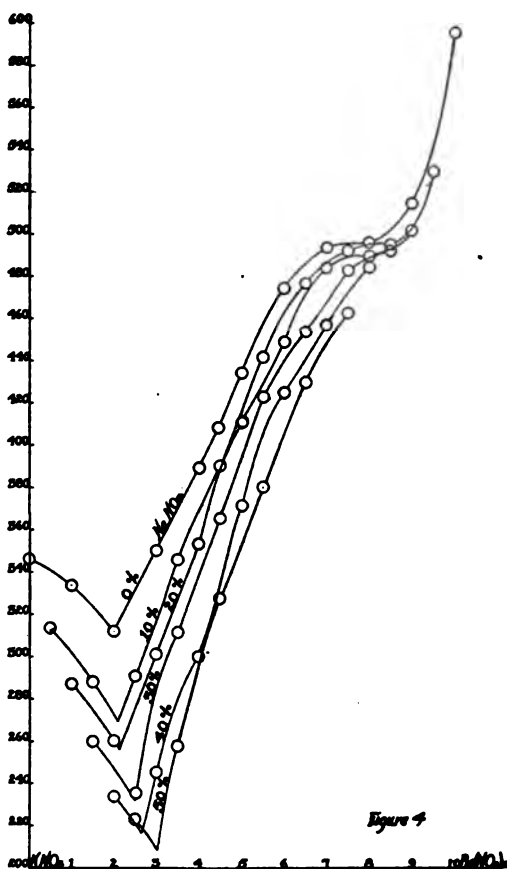


Figure 4

(2) The System Strontium, Sodium and Potassium Nitrates.

With the eutectic point of the system just studied as a guide, the melting points of twelve ternary mixtures of strontium, sodium, and potassium nitrates were determined in the search for the ternary eutectic point. Point number 8 with a composition of 41 equivalent per cent. of NaNO_3 , 50 of KNO_3 and 9 of $\text{Sr}(\text{NO}_3)_2$ was found to solidify practically

¹ Menzies and Dutt, *Loc. cit.*, p. 1370.

² *J. Phys. Chem.*, 2, 209 (1898).

³ *J. Chem. Soc.*, 33, 273 (1878).

⁴ *Bull. soc. chim.*, [2] 47, 300.

⁵ *Compt. rend.*, 97, 45, 1215 (1883).

⁶ *Phil. Mag.*, [5] 17, 462 (1884).

without change of temperature at 208.4° . This result was further verified by determining the melting point of every possible mixture around it and varying from its own composition by only one equivalent per cent. The twelve points are tabulated as follows:

TABLE II.

No.	Eq. % NaNO ₃ .	Eq. % KNO ₃ .	Eq. % Sr(NO ₃) ₂ .	Wt. of NaNO ₃ .	Wt. of KNO ₃ .	Wt. of Sr(NO ₃) ₂ .	Freezing point.
1.....	40	45	15	8	10.70	3.74	254.2
2.....	50	40	10	10	9.51	2.49	221.8
3.....	41	49	10	8.2	11.66	2.49	210.0
4.....	40	50	10	8	11.89	2.49	209.5
5.....	39	51	10	7.8	12.13	2.49	210.5
6.....	30	60	10	6	14.27	2.49	226.8
7.....	42	49	9	8.4	11.66	2.24	209.0
8.....	41	50	9	8.2	11.89	2.24	208.4
9.....	40	51	9	8	12.13	2.24	209.3
10.....	42	50	8	8.4	11.89	1.99	210.0
11.....	41	51	8	8.2	12.13	1.99	211.2
12.....	45	50	5	9	11.89	1.25	213.8

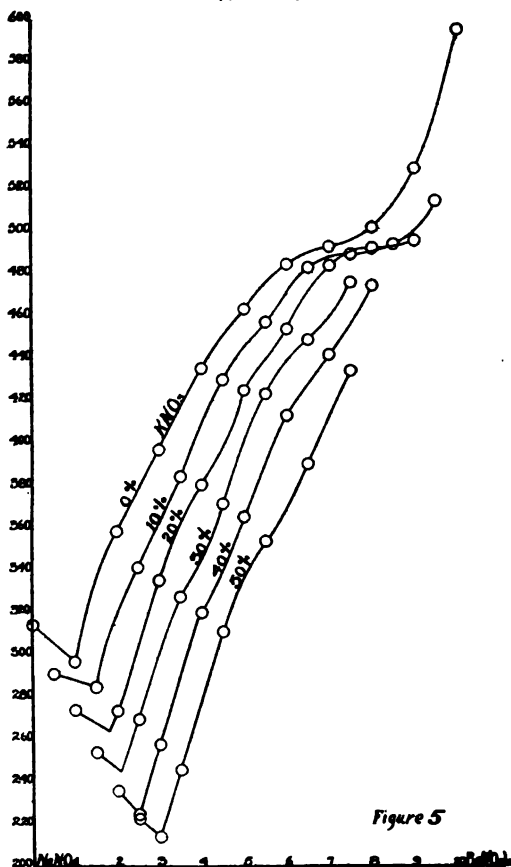


Figure 5

The freezing points are shown on their proper points in Fig. 7. Their numbers run in order on the triangle from top to bottom and left to right. Only a competent triangle of the complete system is used, the base representing zero concentration of $\text{Sr}(\text{NO}_3)_2$.

These twelve ternary points involve no repetitions of other work done. Determinations of single binary points of $\text{Sr}(\text{NO}_3)_2$ with equal weights of NaNO_3 and KNO_3 , respectively, were made by Maumené¹ and the eutectic mixture with KNO_3 was found by Guthrie¹ to contain 25.81% of $\text{Sr}(\text{NO}_3)_2$.

Comparison of the Ternary Systems of Calcium, Barium and Strontium Nitrates with NaNO_3 and KNO_3 .

We are now in a position to make a comparison of three

¹ Loc. cit.

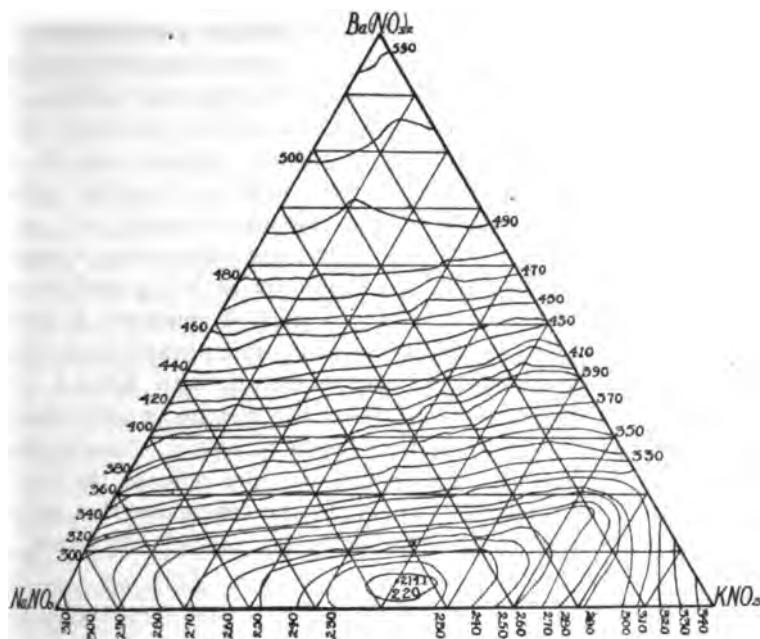


Figure 6

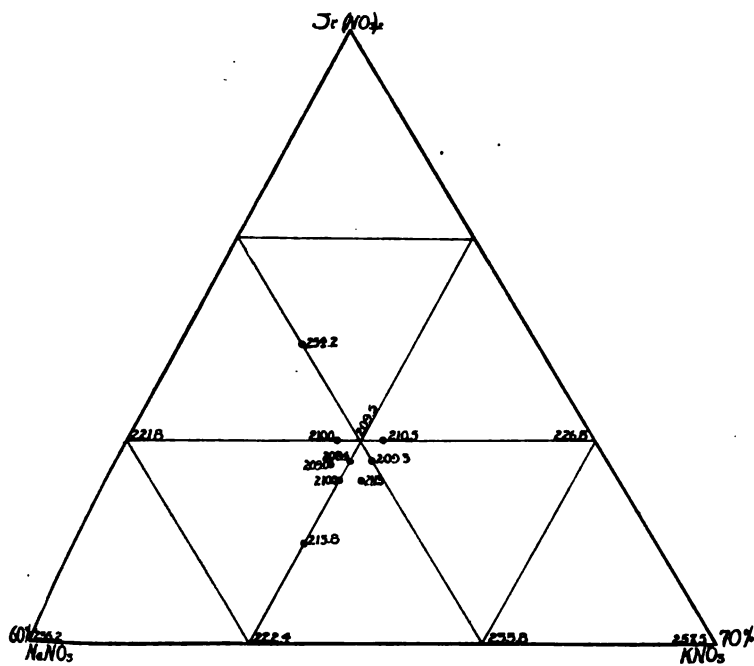


Figure 7

ternary systems, each containing one of the alkaline earth nitrates. The relative position of the three eutectics is best shown diagrammatically as in Fig. 8, using the value obtained by Menzies and Dutt with $\text{Ca}(\text{NO}_3)_2$. It is to be expected, of course, that this system would show the lowest eutectic point and the barium nitrate one of the highest, judging from the melting points of the pure components. For $\text{Ca}(\text{NO}_3)_2$, Carnelley¹ obtained 561° ; for $\text{Sr}(\text{NO}_3)_2$, Ramsay and Eumorfopoulis² found 570° ; and for $\text{Ba}(\text{NO}_3)_2$ the writer found 595.53° . For these values alone it would be further expected, however, that the eutectic for $\text{Sr}(\text{NO}_3)_2$ would be much closer to the one found for $\text{Ca}(\text{NO}_3)_2$. Such a tendency is probably overcome by the fact that strontium and potassium nitrates have a slightly higher eutectic point than even barium nitrate with KNO_3 .³ Consequently the pits in the liquidus surfaces of the systems in which $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ are components differ in depth by only 5.3° and in relative position on the triangle by only 4 equivalent per cent. of the two components, respectively. Such facts point to the conclusion that the contour maps of the two must resemble each other very closely indeed.

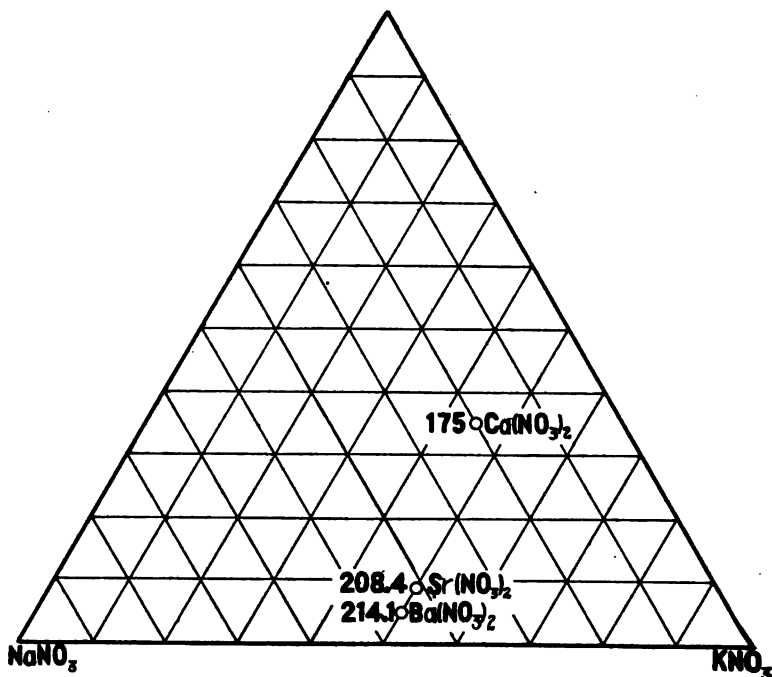


Figure 8

¹ *Loc. cit.*² *Phil. Mag.*, [5] 47, 360 (1896).³ Guthrie, *Loc. cit.*

(3) The System Barium, Lithium and Potassium Nitrates.

The factor of salt stability enters strongly into determinations upon this system—so strongly in fact that the melts of no three-component mixtures with a higher barium nitrate concentration than 10 equivalent per cent. were attempted. There was no difficulty in determining all points on the $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$ and $\text{LiNO}_3\text{-KNO}_3$ sides of the triangle. The eutectic mixtures of lithium and barium nitrates proved to contain only about one equivalent per cent. of the latter, and when 10% was present, the freezing point was observed to be almost 50° higher than the value for pure LiNO_3 . It was possible to reach a point represented by the concentrations 60 equivalents of LiNO_3 and 40 of $\text{Ba}(\text{NO}_3)_2$, freezing at 436.6° before any great decomposition was noted. Immediately a ternary mixture containing 10% of $\text{Ba}(\text{NO}_3)_2$ was tried; however, a vigorous evolution of oxygen began long before a completely melted state had been reached, which was most marked when from 10–40% of the LiNO_3 was present. The melts rapidly became bright yellow from oxides of nitrogen, and crystallization occurred in stages. Tests showed that practically pure $\text{Ba}(\text{NO}_3)_2$ would first separate while the remaining liquid would solidify at a point at least 20° lower. To illustrate the power of a mixture of $\text{Ba}(\text{NO}_3)_2$ and KNO_3 to lower the temperatures where marked decomposition of LiNO_3 begins, a mixture containing about 46 equivalent per cent. each of the first two salts and 8 of the latter was melted. At 266° the evolution of oxygen was very marked, while Carveth¹ found that with pure LiNO_3 apparent decomposition does not begin until a temperature 24° higher (290°) is reached.

The determination of any more than a small portion of the liquidus surface of the ternary system in open tubes is clearly out of the question

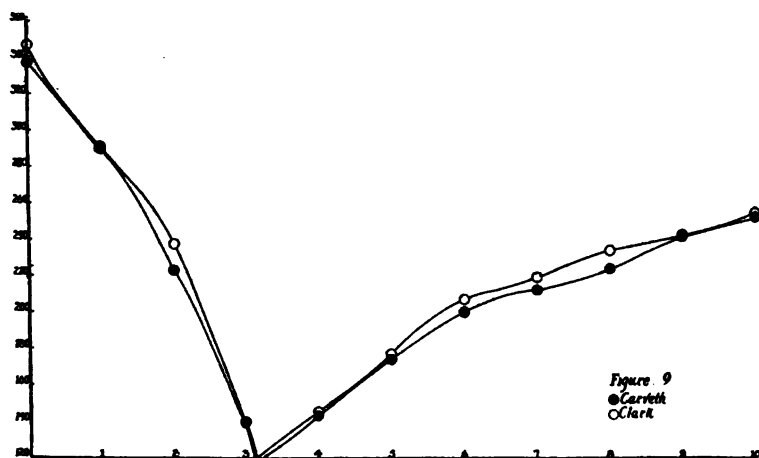


Figure 9
● Carveth
○ Clark

¹ Loc. cit.

when the melted salts show such marked decomposition as that observed. It was deemed advisable, however, to determine the binary curve for LiNO_3 and KNO_3 . A comparison is made in Fig. 9 with the curve as plotted from the results obtained by Carveth¹ in his work on the system Na, K, and Li, the melting points of which were possibly as high as 2° in error. A recrystallized neutral sample of LiNO_3 was used to determine the freezing point of the pure salt. Measurement with the resistance thermometer gave a value of 254.1° as compared with 264° (Carnelley)¹ and 253° (Carveth). In the following table, percentages are equivalent, except for the LiNO_3 - KNO_3 values which are by weight in order to compare with Carveth's curve. Only points which were determined without great difficulty are given:

TABLE III.

No.	Wt. % KNO_3	Wt. % LiNO_3	Wt. g. KNO_3	Wt. g. LiNO_3	Freezing point.
1.....	100	0	30	0	346.1
2.....	90	10	27	3	290.9
3.....	80	20	24	6	237.1
4.....	70	30	21	9	139.8
5.....	60	40	18	12	145.2
6.....	50	50	15	15	177.4
7.....	40	60	12	18	207.0
8.....	30	70	9	21	219.8
9.....	20	80	6	24	234.2
10.....	10	90	3	27	242.3
11.....	0	100	0	30	254.1

TABLE IV.

No.	Eq. % KNO_3	Eq. % LiNO_3	Eq. % $\text{Ba(NO}_3)_2$	Wt. KNO_3	Wt. LiNO_3	Wt. $\text{Ba(NO}_3)_2$	Freezing point.
1.....	0	90	10	0	24.79	5.21	303.17
2.....	0	80	20	0	20.36	9.64	364.4
3.....	0	70	30	0	16.56	13.44	403.58
4.....	0	60	40	0	13.26	16.74	436.6
5.....	10	10	80	3	16.40	3.88	299.09
6.....	20	10	70	6	14.35	3.88	310.37
7.....	30	10	60	9	12.30	3.88	317.92
8.....	40	10	50	12	10.25	3.88	303.70

In conclusion, the writers wish to express their thanks to Mr. W. A. Roberts for assistance in the use of the resistance thermometer.

A grant of two hundred dollars from the Wolcott Gibbs Fund of the National Academy of Sciences has been expended in the purchase of a potentiometer and a galvanometer which will be used in the continuation of the work on fused salts, and also for a study of the lowerings of the freezing points in aqueous solutions of the cobaltamines, and of mixtures of salts. The potentiometer was designed for this work by Dr. W. P. White of the Geophysical Laboratory.

CHICAGO, ILL.

¹ *Loc. cit.*

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE DETERMINATION OF FERROUS IRON IN SILICATES BY TITRATION WITH DICHROMATE.

BY O. L. BARNEBEY.

Received May 31, 1915.

The permanganate titration has been used for the determination of ferrous iron in silicates almost, if not quite, exclusively. This study introduces dichromate for this purpose in a method which is proven to be accurate.

A dichromate titration of the ferrous iron obtained by extraction of a silicate with hydrofluoric acid has several points in its favor. A dichromate solution is more stable than the permanganate solution, which is ordinarily used for this purpose. Moderate quantities of hydrochloric acid do not interfere with the dichromate titration, thus allowing the use of this acid, if it is desired, in the extraction process. Dichromate is not as easily reduced by organic matter as is permanganate. However, ferrous iron cannot be titrated accurately with dichromate in a hydrofluoric acid solution. Further, ferrous iron in fluoride solution oxidizes so rapidly that a slow titration, such as accompanies the use of an outside indicator on a spot plate, may introduce a considerable error.

Boric acid¹ has been found to remove hydrofluoric acid from solution, interaction forming metafluoboric acid. The use of boric acid also permits an accurate titration of ferrous iron to be made with dichromate (Table I).

In Experiments 3 and 4 the dichromate was added until, upon placing a drop of the solution in contact with a drop of 0.05% potassium ferricyanide solution, the development of color on the spot plate was very slow. The time required for the development of the ferrous iron test is designated in the table. More dichromate was then added and another test applied. The more the dichromate added the longer became the time required for the development of the color test. These two experiments show that an enormous error may be introduced by the presence of fluorides. In Experiments 5 and 6 boric acid was present and hydrochloric acid absent. In 7 and 8 boric acid was added previous to titration in the presence of hydrochloric acid. Excellent results were obtained in the four experiments. Constant quantities of iron in the presence of constant amounts of hydrochloric acid in constant volume of solution were titrated with variable amounts of hydrofluoric acid both with and without the addition of boric acid in excess preceding titration (Experiments 9-20 inclusive). Below approximately 0.15 *N* the effect of hydrofluoric acid is found to be small when titrating moderate amounts of iron. Above 0.15 *N* the error becomes progressively larger as the concentration of the

¹ Barnebey, *THIS JOURNAL*, 37, 1481 (1915).

TABLE I.—TITRATION OF IRON WITH DICHROMATE IN HYDROCHLORIC AND HYDROFLUORIC ACID SOLUTIONS.

1 cc. $K_2Cr_2O_7$ = 0.006381 g. FeO .¹1 cc. $FeSO_4$ = 1.007032 g. FeO .

	Normality.		Volume. Cc.	G. FeO .			Time for development of color. Min.
	HCl.	HF.		Present.	Found.	Error.	
1.....	0.50	..	200	0.2110	0.2110	+0.0000	1
2.....	..	0.125	200	0.2110	0.2108	-0.0002	1
3.....	..	0.625	200	0.2110	0.1914	-0.0196	0.5
					0.2067	-0.0043	2
					0.2074	-0.0036	3
					0.2080	-0.0030	7
4.....	..	3.125	200	0.2110	0.1659	-0.0451	0.5
					0.1789	-0.0321	1
					0.1914	-0.0196	2
					Found.		
					Without H_2BO_3 .	With H_2BO_3 .	
5.....	..	0.125	200	0.2110	..	0.2111	1
6.....	..	0.500	200	0.2110	..	0.2110	1
7.....	0.50	0.125	200	0.2110	..	0.2110	1
8.....	0.50	0.625	200	0.2110	..	0.2109	1
9.....	0.50	0.05	200	0.1567	0.1563	..	1
10.....	0.50	0.10	200	0.1567	0.1566	..	1
11.....	0.50	0.15	200	0.1567	0.1564	..	1
12.....	0.50	0.25	200	0.1567	0.1557	0.1567	1
13.....	0.50	0.40	200	0.1567	0.1552	0.1566	1
14.....	0.50	0.50	200	0.1567	0.1548	0.1567	1
15.....	0.50	0.75	200	0.1567	0.1528	0.1568	1
16.....	0.50	1.00	200	0.1567	0.1492	0.1566	1
17.....	0.50	1.50	200	0.1567	0.1425	0.1567	1
18.....	0.50	2.00	200	0.1567	0.1415	0.1568	1
19.....	0.50	2.50	200	0.1567	0.1400	0.1566	1
20.....	..	2.50	200	0.1567	..	0.1566	1

hydrofluoric acid increases. The addition of boric acid removes this fluoride effect and permits excellent results to be obtained even when the concentration of the hydrofluoric acid is 2.5 *N*.

Sensitiveness of the Ferricyanide Test for Ferrous Iron.

In previous work the author has frequently observed that variation of the strength of hydrochloric acid has a tendency to change the sensitiveness of the ferricyanide test for small amounts of ferrous iron. To ascertain the extent of this effect a series of experiments was performed (Table II). The effect of hydrofluoric acid was also made a matter of study in this series. In each experiment the acid, with or without added ferric chloride, was diluted to 200 cc. volume and standard ferrous sulfate added

¹ The dichromate solutions used in this work were standardized against pure electrolytic iron and the ferrous iron solutions were standardized with the dichromate in each series of experiments, using ferricyanide as indicator.

until one drop of the solution gave the color test with ferricyanide on a porcelain spot plate.

The column "test sensitiveness" gives the sensitiveness computed upon the basis of actual parts of ferrous iron contained in the solution. In order to obtain the sensitiveness in the spot plate reaction the "test sensitiveness" results should be multiplied by twenty, inasmuch as twenty drops of the solution were equivalent to one cc. and only a single drop of the solution was removed for the test with ferricyanide. One minute was the time allowed for the color to develop. Preliminary study had indicated that not less than 0.04 or more than 0.10% potassium ferricyanide gives the best results in the test for ferrous iron. In the tests here recorded three series of tests were used as checks upon each other, involving the use of 0.04, 0.06 and 0.08% potassium ferricyanide solutions.

TABLE II.—SENSITIVENESS OF THE FERRICYANIDE TEST FOR FERROUS IRON.

1 cc. $\text{FeSO}_4 = 0.005222 \text{ g. Fe.}$

	Normality.		0.1 N FeCl_3 Cc.	Volume. Cc.	G. Fe required.	Test sensi- tiveness. One part in
	HCl.	HF.				
1.....	200	0.0002	1,000,000
2.....	0.30	200	0.0005	400,000
3.....	0.60	200	0.0010	200,000
4.....	1.20	200	0.0019	105,000
5.....	1.60	200	0.0025	80,000
6.....	3.20	200	0.0060	33,000
7.....	..	0.05	..	200	0.0020	100,000
8.....	..	0.15	..	200	0.0045	44,000
9.....	..	0.25	..	200	0.0068	30,000
10.....	..	0.50	..	200	0.0094	21,000
11.....	..	1.25	..	200	0.0151	13,000
12.....	..	2.50	..	200	0.0234	8,500
13.....	200	0.0002	1,000,000
14.....	0.25	..	5	200	0.0003	670,000
15.....	0.50	..	5	200	0.0002	1,000,000
16.....	1.00	..	5	200	0.0002	1,000,000
17.....	2.50	..	5	200	0.0004	500,000
18.....	..	0.05	5	200	0.0003	670,000
19.....	..	0.10	5	200	0.0008	250,000
20.....	..	0.25	5	200	0.0022	90,000
21.....	..	0.50	5	200	0.0104	19,000
22.....	..	1.00	5	200	0.0135	15,000
23.....	..	2.50	5	200	0.0140	14,000
24.....	..	0.50	10	200	0.0025	80,000
25.....	..	1.00	10	200	0.0059	34,000
26.....	..	0.50	40	200	0.0010	200,000
27.....	..	1.00	40	200	0.0020	100,000

Experiments 1-6 and 7-12 show a progressive lowering of the sensitiveness of the ferrous iron test as the normality of the hydrochloric and hydrofluoric acid increases. However, the addition of ferric iron to the

solution (Experiments 14-27) permits a more accurate test to be made. (The ferric chloride was entirely free from any trace of ferrous iron.) Sulfuric and phosphoric acids give an effect similar to hydrochloric acid. Using 2.5 *N* sulfuric acid, 0.004 g. of iron was required in 200 cc. vol. to give the ferrous iron test on the spot plate. This corresponds to a solution sensitiveness of one part in fifty thousand and a spot plate sensitiveness of one part in a million. With 2.5 *N* phosphoric acid (computed on the basis of three replaceable hydrogen atoms), 0.006 g. of iron was necessary, corresponding to one part in thirty-three thousand and six hundred sixty thousand parts for the solution and spot plate sensitiveness, respectively. The addition of ferric chloride to the solution or spot plate, especially the latter, brings out the test with a very small amount of ferrous iron, 0.0002 g. being easily detected, hence yielding a solution sensitiveness of one part in a million and a spot plate sensitiveness of one part in twenty million parts of solution. Other salts such as sodium, ammonium, potassium, barium and aluminum chlorides do not have an effect similar to ferric chloride. It does not seem improbable that the ferrous chloride in strong acid solution reduces in part the ferri- to ferrocyanide.¹ The ferrocyanide then reacts with the ferric iron present to form a salt similar to or identical with "Prussian Blue." "Prussian Blue" has a tendency to decompose in hydrochloric acid solution forming ferric chloride and hydroferrocyanic acid. Now the addition of ferric iron to such a solution tends to form a ferri-ferrocyanide by mass action, hence causing the color to reappear. When the hydrochloric acid is weak the reaction on the spot plate proceeds normally, yielding a ferrous ferricyanide. However, the reactions are undoubtedly complex in character, as indicated by the differences of colors, green to blue, obtained on the spot plate. It matters not which blue or greenish blue is formed if the appearance of color can be obtained by the presence of a very slight excess of ferrous iron in such a manner as to constitute a reliable test.

The effect of diminishing sensitiveness of the ferrous iron test in strong hydrochloric and hydrofluoric acid solutions was tried in the titration of small amounts of iron. In this series of experiments the standard solutions of ferric chloride, ferrous chloride and potassium dichromate were approximately 0.1 *N* (Table III).

In the presence of 2.5 *N* hydrochloric acid small amounts of ferrous iron cannot be titrated directly with accuracy (Experiments 1, 4, 5 and 8). Experiments 2, 6 and 9 show that the addition of ferric chloride to the solution of ferrous iron permits a correct titration to be made, even when the hydrochloric acid is 2.5 *N*. As the quantity of ferrous iron to be titrated increases, thus forming more ferric iron in solution, the titration becomes more accurate. Experiments 11, 12, 13 and 14 indicate that

¹ See also Hofmann, Heine and Höchteln, *Ann.*, 337, 1 (1904).

TABLE III.—EFFECT OF STRONG HYDROCHLORIC AND HYDROFLUORIC ACIDS ON THE TITRATION OF SMALL AMOUNTS OF FERROUS IRON.

	Normality.		0.1 N FeCl. Cc.	G. Fe.		
	HCl.	HF.		Present.	Found.	Error.
1.....	2.50	0.0057	0.0027	—0.0030
2.....	2.50	..	10	0.0057	0.0055	—0.0002
3.....	0.25	0.0057	0.0057	±0.0000
4.....	2.50	0.0113	0.0064	—0.0049
5.....	2.50	0.0170	0.0156	—0.0014
6.....	2.50	..	10	0.0170	0.0170	±0.0000
7.....	0.25	0.0170	0.0170	±0.0000
8.....	2.50	0.0284	0.0275	—0.0009
9.....	2.50	..	10	0.0284	0.0285	+0.0001
10.....	0.25	0.0284	0.0282	—0.0002
11.....	2.50	0.0567	0.0564	—0.0003
12.....	2.50	0.0567	0.0565	—0.0002
13.....	2.50	0.1134	0.1135	+0.0001
14.....	2.50	0.1134	0.1135	+0.0001
15.....	0.50	0.0284	0.0285	+0.0001
16.....	0.50	0.0567	0.0565	—0.0002
17.....	0.50	0.1418	0.1416	—0.0002
18.....	0.50	0.2268	0.2268	±0.0000
19.....	..	0.25	..	0.0057	0.0004	—0.0053
20.....	..	0.25	5	0.0057	0.0020	—0.0037
21.....	..	0.25	1	0.0057	0.0054	—0.0003
22.....	..	0.25	..	0.0113	0.0074	—0.0039
23.....	..	0.25	5	0.0113	0.0088	—0.0025
24.....	..	0.25	1	0.0113	0.0113	±0.0000
25.....	..	0.50	..	0.0113	0.0034	—0.0079
26.....	..	0.50	5	0.0113	0.0074	—0.0039
27.....	..	0.50	1	0.0113	0.0114	+0.0001
28.....	..	1.00	..	0.0113	0.0000	—0.0113
29.....	..	1.00	5	0.0113	0.0025	—0.0088
30.....	..	1.00	1	0.0113	0.0084	—0.0029
31.....	..	2.00	5	0.0113	0.0004	—0.0109
32.....	..	2.00	1	0.0113	0.0059	—0.0054
33.....	..	2.50	H ₂ BO ₃ Added	0.0057	0.0057	±0.0000
34.....	..	2.50	" "	0.0113	0.0114	+0.0001
35.....	..	2.50	" "	0.0170	0.0171	+0.0001
36.....	..	2.50	" "	0.0284	0.0286	+0.0002
37.....	..	2.50	" "	0.0284	0.0286	+0.0002
37.....	..	2.50	" "	0.0567	0.0570	+0.0003

amounts of ferrous iron above 0.05 to 0.10 g. can be titrated in even 2.5 N hydrochloric acid with safety. Experiments 15, 16, 17 and 18 show that 0.50 N acid is not detrimental when above 0.03 g. of iron is being titrated. With less concentrations of acid much less ferrous iron could be accurately determined. The addition of ferric chloride to the fluoride solution has a tendency to improve the accuracy of the titration, yet not to a sufficient

¹ Drops of the ferric chloride solution were added to the ferricyanide on the spot plate.

degree to make the titration reliable (Experiments 19-32). The addition of a drop of ferric chloride to each drop of indicator on the spot plate before or after adding the drop of solution to be tested gave a much more accurate result in Experiments 21, 24, 27, 30 and 32. However, this required careful observance for the end point, which was a trifle obscure because of a very slight green tinge remaining after the titration was completed. However, the addition of boric acid removes the hydrofluoric acid, thus permitting an accurate titration of small amounts of ferrous iron to be made the same as when larger amounts are involved (Experiments 33-37, see Table I).

From the preceding work it is recommended that not more than 5 or at the most 10 cc. of concentrated hydrochloric acid be present in a volume of 200 cc. when small amounts of iron are to be titrated. Inasmuch as the use of 10 cc. has no advantage over 5 cc., the latter amount should be employed. Boric acid when added to solutions containing hydrofluoric acid removes the latter and permits a quantitative determination of the iron to be made, whether the iron is present in small or large amounts.

Analysis of Silicates for Ferrous Iron.

In a previous article¹ ferrous iron solutions containing fluoboric acid were shown to be quite stable in the presence of the air. Since the use of boric acid permits a correct titration to be made, the method previously outlined² can be modified, using dichromate instead of permanganate for the standard oxidizing solution. In Series IV the samples were decomposed according to the method referred to above, using 10 cc. of hydrochloric acid, sp. gr. 1.2 (sulfuric acid can be used if desired), and 10 to 20 cc. of hydrofluoric acid of 48% strength. A convenient strength of dichromate was found to be 1 cc. = 0.001 g. FeO. A 0.05% solution of potassium ferricyanide was used as indicator on a spot plate, one drop being placed on each spot. When the end point had apparently been reached, two or three drops of the solution being titrated were used for the final test for ferrous iron in the spot plate reaction, thus increasing the accuracy of the test.

TABLE IV.—ANALYSIS OF SILICATES FOR FERROUS IRON.

Silicate number.	Sample Grams.	Per cent. FeO found by	
		KMnO ₄ .	K ₂ Cr ₂ O ₇ .
1.....	1	1.10	1.02
2.....	2	0.51	0.51
3.....	1	13.80	13.70
4.....	1	14.41	14.38
5.....	1	6.49	6.40
6.....	1	5.47	5.47

¹ Barnebey, THIS JOURNAL, 37, 1191 (1915).

² Loc. cit.

In the analysis of Samples 1 and 2 the solutions had to be filtered to remove suspended organic matter in order to permit titration with permanganate, yet no trouble was encountered in titrating with dichromate without filtration. Samples 3-6 inclusive did not contain organic matter. All of these results are average results of closely agreeing duplicating analyses.

Conclusions.

1. The concentration of acid should be small when titrating small amounts of iron with dichromate, using ferricyanide as indicator on the spot plate. If the concentration is quite large ferric chloride should be added to give a sharper color change on the spot plate.
2. Boric acid counteracts the influence of hydrofluoric acid in the dichromate titration of ferrous iron and hence addition of this reagent to the hydrofluoric acid extraction of the silicate yields a solution in which the ferrous iron can be accurately titrated with dichromate, using ferricyanide as indicator on a spot plate.

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NOTE.

Use of Acetone for Drying Chemical Utensils.—Acetone is miscible in all proportions with water. It has a boiling point of 56° . On account of these two properties acetone is an excellent substance to use as a wash to facilitate the drying of glassware, especially flasks, bottles, etc. After cleaning and rinsing with water the vessel is allowed to drain a short time, then sufficient acetone is added to give a good wash. After again draining a few seconds the remaining acetone is removed by drawing air through the vessel by inserting a glass tube which is connected to suction, or by the application of heat. The author has found the use of acetone very serviceable, replacing the use of alcohol to remove the water, then ether to remove the alcohol. The acetone has the merit of being cheaper than either alcohol or ether at the present time.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SOUTH DAKOTA.]

DERIVATIVES OF PHENYL ETHER.

BY ALFRED N. COOK AND FRANK F. SHEERWOOD.

Received June 9, 1915.

2-Nitro-4'-methyl phenyl ether ($\text{NO}_2\cdot\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\cdot\text{CH}_3$) was first prepared by one of the authors¹ of this paper about sixteen years ago and some of its derivatives were prepared and studied. Subsequently some other compounds of an analogous nature and corresponding derivatives

¹ *Am. Chem. J.*, 24, 525-529 (1900).

were prepared and described. Since the first paper was not as comprehensive as those that appeared subsequently, it was thought that a further study of the above-mentioned compound would be of some interest and profit.

The method here used was somewhat varied and shortened in the light of subsequent experience and as a consequence the yield was somewhat increased. *o*-Bromo-nitro benzene, with somewhat more than the theoretical equivalent of potassium cresolate, was warmed on an oil bath to 125° until all action had ceased. The temperature was then gradually raised to 160°. The potassium cresolate employed was also prepared somewhat differently than in the first instance, with the result that a much whiter and better product was obtained, which was probably one factor in the increased yield. No water was added to the mixture of potassium hydroxide and *p*-cresol. The two substances were simply mixed and then heated on the water bath until as dry as possible. The drying was then completed in the air bath at about 110° for a short time. Care must be exercised in the final heating, since, if the heat is applied too long, the substance begins to char and the final product is not so good.

The nitro-methyl phenyl ether was purified by fractional distillation *in vacuo* several times and subsequent crystallization from alcohol. In spite of the fact that an excess of potassium phenolate was always employed in its preparation there always remained behind some unchanged nitro-bromo benzene to contaminate the product. Apparently also there was always some by-product formed which, however, was not studied. The above method of purification was found to be much better and more expedient than the one formerly employed. The compound boiled at 210° under a pressure of 15 mm. and melted at 49°, the same as first¹ determined.

A hexa-nitro-methyl phenyl ether ((NO₂)₆.CH₃.C₁₂H₃) was obtained by treating the mother substance with concentrated nitric acid at the temperature of the boiling water bath. The reaction takes place very slowly and it is necessary to heat for some time before solution takes place. The acid solution was poured into a large amount of water, when the nitro-compound was precipitated as a viscous mass, which, on stirring for several minutes, completely solidified. It is very soluble in hot alcohol and but sparingly soluble in cold alcohol. It is soluble in benzene, ether, carbon disulfide and sparingly soluble in water. After crystallization from alcohol several times it melted at 103.5°.

Analyses for nitrogen yielded 18.13% and 18.22%, respectively. Theory, 18.55%.

On account of the small yield obtained it was thought that a part of the substance might have remained behind in the acid solution. On greatly diluting the solution, however, no further precipitation took place.

¹ *Loc. cit.*

but on neutralizing the acid solution with caustic soda a second crop of crystals separated out on standing, which were of a higher degree of purity than the first crop. A considerable portion of the substance remained behind in solution in the water, since the substance is slightly soluble in water. A hexa-nitro compound was prepared by the senior author of this paper some years ago¹ by nitrating 4-nitro-4'-methyl phenyl ether in an analogous manner. Its melting point was not determined, but its other properties are identical with those of this compound. With little doubt I think the two compounds are identical.

Bromo-2-nitro-4'-methyl phenyl ether ($\text{Br}.\text{NO}_2.\text{CH}_3.\text{C}_{12}\text{H}_7\text{O}$) was prepared by dissolving 2-nitro-4'-methyl phenyl ether in carbon disulfide, adding a small crystal of iodine to act as a catalytic agent or carrier for the bromine, and then a large excess of bromine and allowing to stand two or three days. After evaporating off the carbon disulfide and distilling under diminished pressure, the compound was purified by crystallizing from alcohol several times, when it melted at 23° . It is a yellow-colored substance, very much resembling the mother substance from which it was prepared.

Two analyses for bromine yielded 34.18% and 34.3%, respectively. Theory requires 34.6%.

Bromo-2-amino-4'-methyl phenyl ether ($\text{Br}.\text{NH}_2.\text{CH}_3.\text{C}_{12}\text{H}_7\text{O}$) was obtained by reducing the bromine derivative of the mother substance with tin and hydrochloric acid in alcoholic solution while warming on the water bath and subsequent separation of the tin with hydrogen sulfide and evaporating to crystallization. The compound is quite stable and yields a *free base* with caustic alkalis which is likewise quite stable. With platonic chloride it yields a *chloroplatinate* which crystallizes in brilliant reddish crystalline grains.

Platinum found, 20.22%. Theory requires 20.00%.

2-Nitro-4'-methyl phenyl ether sulfonic acid ($\text{NO}_2.\text{CH}_3.\text{C}_{12}\text{H}_7.\text{SO}_3\text{H}$) was prepared by precipitating the lead of the lead salt with hydrogen sulfide and evaporating to crystallization. It is of a yellow color and fumes in the air when warmed on the water bath even when dissolved in considerable water. On bringing the open mouth of a bottle containing ammonium hydroxide near the warmed acid dense, white clouds are formed similar to those formed by ammonia and hydrochloric acid. When aspirated with a current of air in water solution, or in the dry state into a second tube containing distilled water for a couple of hours, sufficient acid passed over to yield a test with litmus and affect the sense of taste. Of the various salts prepared none were found to contain any water of crystallization. This acid, therefore, differs from all of the other analogous acids so far prepared, since one or more of the salts of all of the other sul-

¹ THIS JOURNAL, 25, 64 (1903).

fonic acids contain from one to several molecules of water of crystallization. The acid causes various carbonates to effervesce. The composition of this acid is sufficiently shown by the analysis of several of its salts.

2-Amino-4'-methyl phenyl ether sulfonic acid ($\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$) was prepared by reducing the corresponding copper salt of the sulfonic acid in water solution with tin and hydrochloric acid while warming on the water bath, removing the tin by means of hydrogen sulfide, and evaporating to crystallization. Although it is both base and acid it possesses fairly pronounced acid properties. It causes the effervescence of carbonates.

Lead-2-nitro-4'-methyl phenyl ether carbonate was prepared by dissolving the mother substance in a small quantity of sulfuric acid containing a small quantity of sulfur trioxide, adding to a large amount of water, treating with lead carbonate until effervescence ceases, filtering and evaporating to crystallization. The lead salt thus prepared seemed to be quite difficult to purify and persisted in giving abnormally high results for lead for a long time.

Pb found after repeated crystallization, 25.2%. Theory, 25.15%.

The barium salt was prepared in an analogous manner as in the case of the lead salt with the substitution of barium carbonate. It is of a slightly yellow color, very soluble in hot water and but slightly so in cold water, and comparatively easy to purify. It contains no water of crystallization. It crystallized in radial aggregations so characteristic of the compounds of phenyl ether so far prepared.

Barium found, 15.4%. Theory, 15.15%.

The strontium salt was prepared similarly to the barium and lead salts with the substitution of strontium carbonate. It is of a light yellow color and contains no water of crystallization.

Found 12.29% and 12.18% of strontium, respectively. Theory, 12.45%.

The copper salt was prepared by adding the calculated amount of copper sulfate to the barium salt to completely precipitate the barium and evaporating to crystallization. It is quite sparingly soluble in water, from which it crystallizes on cooling in a very bulky mass. When moist the salt is of a nearly white color, with perhaps a slight yellow tinge; when dry, however, it possesses a slight greenish tinge. It readily reduces with tin and hydrochloric acid and yields a stable, free base.

The cadmium salt was prepared in the same general manner as the copper salt with the substitution of cadmium sulfate. It is of a yellowish white color, and fairly soluble in water, from which it crystallizes in bulky, radial aggregations. It contains no water of crystallization.

The sodium salt was prepared by precipitating the barium of the barium

salt by means of sodium carbonate and evaporating to crystallization. It is of a light yellow color and very soluble in water.

Sulfur found, 9.64% and 9.75%, respectively. Theory, 9.66%.

The compound seemed to be very hard to oxidize, even for a sulfur compound, requiring two full days' heating with fuming nitric acid under pressure at a high heat.

2-Nitro-4'-methyl phenyl ether sulfonchloride ($\text{NO}_2 \cdot \text{CH}_3 \cdot \text{C}_{12}\text{H}_7 \cdot \text{SO}_2\text{Cl}$) was prepared by treating the sodium sulfonate with an excess of phosphorus pentachloride. The two substances were powdered, mixed thoroughly, shaken to insure complete mixing, when an action took place accompanied by a marked rise of temperature, the mixture assuming a semi-pasty condition. Ice water was then poured into the flask and allowed to remain several hours with occasional shaking. The sulfonchloride remained in the bottom of the flask in the form of solid granules and was separated by filtration with suction. The substance is very stable towards water and alcohol. The substance is soluble in alcohol, benzene, and other organic solvents. It crystallizes from alcohol in light yellow plates which melt at 69° (uncor.).

VERMILLION, S. DAK.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

PHENOLS III. THE PREPARATION OF SOME NEW SUBSTITUTED CRESOLS.¹

BY ARTHUR J. HILL AND LOUIS E. GRAF.

Received June 8, 1915.

The work recorded in this paper is a continuation of an investigation on phenols and related compounds which was begun by Johnson and Hodge² in 1913. It is the third paper on this subject and is devoted to the synthesis and description of some new derivatives of *p*-cresol.

Our knowledge regarding the alkyl derivatives of the three isomeric cresols is somewhat limited. While several have been described in the literature, in many cases, however, the position occupied by the substituent alkyl group is held as uncertain.

Only two propyl cresols have been described. One of these, 2-hydroxy-4-propyl-1-methylbenzene, was synthesized by Bayrac,³ who obtained it by alkali fusion of 1-methyl-4-propyl-benzenesulfonic acid. The other, 3-hydroxy-2-normal propyl-1-methylbenzene, was prepared by Mazzara⁴

¹ The experimental work described in this paper was done by Mr. Louis E. Graf in candidacy for the Degree of Master of Science in the Sheffield Scientific School of Yale University.

² THIS JOURNAL, 35, 1014 (1913).

³ Bull. soc. chim., [3] 13, 896 (1895).

⁴ Gazz. chim. ital., 12, 167 (1882).

through the interaction of normal propyl alcohol, *m* cresol and anhydrous magnesium chloride at 200°. In this connection, mention should also be made of Klages'¹ synthesis of the methyl ether of 2-propyl-4-methylphenol (I) which he obtained by the reduction of either 4-methyl-2-propenyl-phenol methyl ether (II) or 1-methoxy-4-methyl-2-propylol benzene (III). A synthesis of the free phenol is now recorded in this paper.

Our information concerning the ethyl substituted cresols is more conflicting than that of the propyl derivatives. Clemmenson² has reduced 3-methyl-4-hydroxy-acetophenone (IV) to 2-methyl-4-ethylphenol (V) by means of zinc-amalgam and hydrochloric acid and characterizes his compound as "das Phenol das bisher noch nicht dargestellt worden war." There is a possibility, however, that this statement is not wholly correct. For example, Bayer & Co.³ have shown that 2-hydroxy- β -ethyl-1-methylbenzene could be synthesized by the interaction of *o*-cresol with ethyl alcohol at 180° in the presence of anhydrous zinc chloride. The boiling point of their product is stated as 220°; that of Clemmenson's is 224° at 740 mm., thus indicating that the two products are possibly identical.

There are also two other ethyl cresols which should be mentioned. These are the so-called " α -" and " β -"phenol derivatives of *p*-ethyl-methylbenzene, which Bayrac⁴ synthesized by fusion of the corresponding " α -" and " β -"sulfonic acids with alkali.

(α -phenol derivative)- β -hydroxy-4-ethyl-1-methylbenzene. B. p. 222.5-226.5°.

(β -phenol derivative)- β -hydroxy-4-ethyl-1-methylbenzene. B. p. 219.8-220.8°.

The sulfonic acids were isolated by Bayrac in the form of their corresponding barium salts, from the reaction product, resulting from the sulfonation of *p*-ethyl-methylbenzene. He did not prove their constitution. Only a small difference in the physical properties of his barium salts was the basis for Bayrac's assumption that he had actually obtained two different sulfonic acids. Neither did he establish the constitution of his " α -" and " β -"phenols, which in physical properties differed from each other only as regards a few degrees in boiling point.

So far as the writers have been able to ascertain, no ethyl or propyl *p*-cresols are listed either in Beilstein's Handbuch, or Richter's "Lexikon der Kohlenstoff verbindungen." We have now synthesized two such representatives of the *p*-cresol series, namely, 2-ethyl-4-methylphenol (VII) and 2-propyl-4-methylphenol (IX) by the action of zinc-amalgam

¹ *Ber.*, 37, 3994 (1904).

² *Ibid.*, 47, 51 (1914).

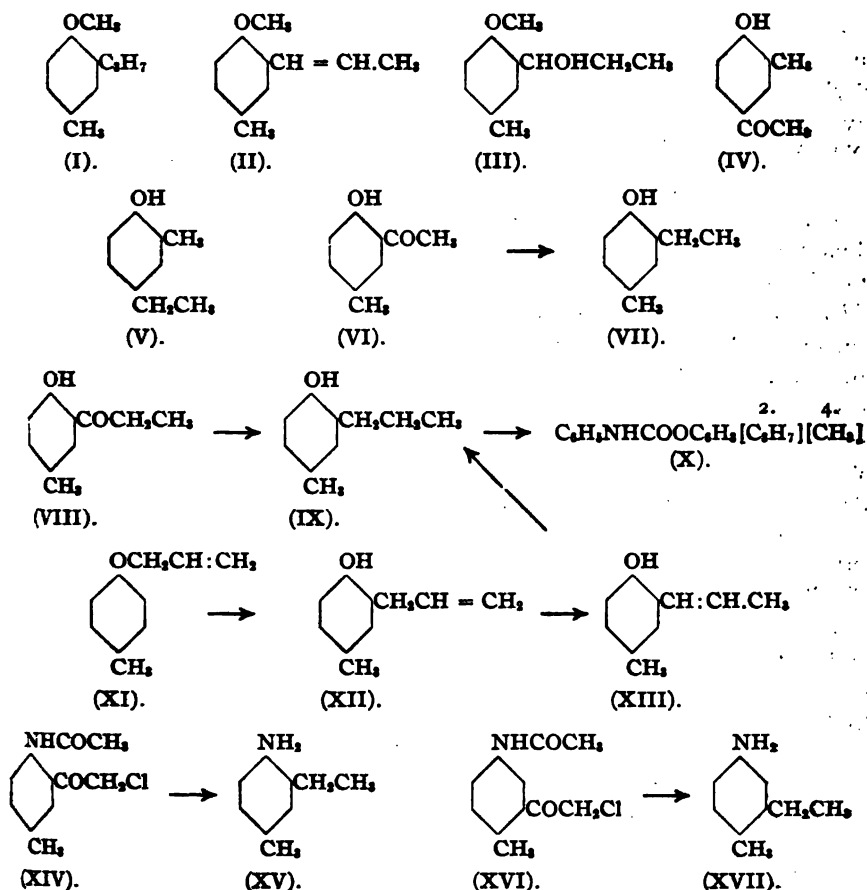
³ D. R. P. 61575.

⁴ *Bull. soc. chim.*, [3] 13, 892 (1895).

and hydrochloric acid on 2-hydroxy-5-methyl-acetophenone (VI) and 2-hydroxy-5-methyl-propiophenone (VIII), respectively.

These ketones have been previously synthesized by Betteridge¹ and Auwers² by the action of aluminium chloride and acetyl and propionyl chlorides, respectively, upon the methyl ether of *p*-cresol in carbon bisulfide solution. We prepared these same ketones, modifying the above procedure to the extent of using petroleum ether as a solvent instead of carbon bisulfide. The physical properties of our compounds were in agreement with those of the ketones described by Betteridge and Auwers.

Of interest regarding the acylation of the *p*-cresol ethers was the fact that Betteridge, using propionyl chloride and aluminium chloride in carbon bisulfide solution, obtained from the ethyl ether of *p*-cresol, the ethyl ether of propionyl-*p*-cresol. The latter he was obliged to demethyl-



¹ Diss., Breslau, 1898.

² Ber., 36, 3891 (1903); 47, 3318 (1914); Ann., 364, 164 (1908).

até according to Gattermann's¹ aluminium chloride method in order to obtain his phenol. We found that on applying the Friedel-Craft reaction in petroleum-ether solution, that demethylation took place during the course of the reaction. We investigated both the methyl and ethyl ethers of *p*-cresol in the reaction with acetyl chloride, and observed both demethylation and de-ethylation to occur. In fact, Auwers² stated in a later paper that acetyl *p*-cresol could be directly obtained from the methyl ether of *p*-cresol with acetyl chloride. The conversion of a phenolic ether into the free phenol is not uncommon under the above-described conditions, although it has been our experience that this reaction is not so liable to occur in petroleum-ether solution.

In order to establish with certainty the position which the acyl groups occupy when substituting in *p*-cresol we proceeded as follows:

p-Cresol was first converted into its allyl ether (XI) and the latter in accordance with Claisen's³ recent method then rearranged into 2-allyl-4-methylphenol (XII) by the application of heat. The allyl derivative was then rearranged into its corresponding propenyl derivative (XIII) by heating with aqueous alkali. We observed that 2-propenyl-4-methylphenol (XIII) would easily reduce to 2-propyl-4-methylphenol (IX) with metallic sodium and alcohol. The product thus obtained was identical with the product resulting from the reduction of 2-hydroxy-5-methyl-acetophenone (VIII) with zinc-amalgam and hydrochloric acid. In sharp contrast to the behavior of 2-propenyl-4-methylphenol (XIII) was the resistance of 2-allyl-4-methylphenol (XII) to reduction with sodium and alcohol. In fact, we were unable to accomplish a reduction of this compound with zinc-amalgam, or even hydriodic acid and phosphorus. This behavior is quite in accord with the previously observed resistance of allyl-substituted phenols to reduction. In fact, Klages states⁴ in his article entitled, "Ueber das Dihydro Anethol," that—

"es bleibt die Frage offen, ob allgemein in Benzol-derivaten die Gruppe $\text{CH} = \text{CH} - \text{CH}_3$ reduzirbar ist, und sich in dieser Hinsicht anders verhält als die Gruppe $\text{CH}_2\text{CH} = \text{CH}_2$."

The reduction products of both 2-propenyl-4-methylphenol (XIII) and 2-hydroxy-5-methyl-propiophenone (VIII) condense with phenyl isocyanate giving the same product, namely, the phenyl urethane of 2-hydroxy-5-methyl-acetophenone (X). *The propionyl group in 2-hydroxy-5-methyl-propiophenone is then in the ortho position in respect to the hydroxyl group.*

Reasoning from analogy we may then assume the structure of 2-hydroxy-

¹ Ber., 25, 3531 (1892).

² Ann., 364, 164 (1908).

³ Ibid., 401, 44 (1913).

⁴ Ber., 32, 1436 (1899).

5-methyl-acetophenone (VI) which was smoothly reduced to 2-ethyl-4-methylphenol (VII).

As a further extension of the application of zinc-amalgam as a reducing agent, it has been of interest to us, in the light of future investigations, to ascertain the reducibility of amido phenyl ketones. We were successful in reducing 3-acetylamido-6-methyl-chloroacetophenone (XVI) and 2-acetylamido-5-methyl-chloroacetophenone (XIV) to 3-ethyl-4-methylaniline (XVII) and 2-ethyl-4-methylaniline (XV), respectively. We definitely established by these reductions the constitution of the above chloroacetophenones described by Kunckell¹ since 2-ethyl-4-methylaniline (XV) has been described by Willgerodt and Brandt² and its constitution established by these same investigators.

The writers wish to acknowledge their indebtedness to Prof. Treat B. Johnson, at whose suggestion these experiments were undertaken.

Experimental Part.

2-Hydroxy-5-methyl-acetophenone, VI.—Thirty-five cc. of acetyl chloride were slowly added to a solution of 30 g. of the methyl ether of *p*-cresol in 200 cc. of dry petroleum ether. Twenty-five grams of aluminium chloride were added as a catalyst. The mixture was then heated for 30 hours on a steam bath. At this time evolution of hydrochloric acid gas had practically ceased. The petroleum ether was then carefully decanted from a dark-colored residue, and the latter poured into ice water, acidulated with hydrochloric acid, in order to decompose the double aluminium compound. The solution was extracted with ether, and the resulting ethereal solution of the phenol carefully washed with sodium carbonate and water, and then dried over calcium chloride. The phenol was distilled at ordinary pressure, sixteen grams being obtained from the fraction boiling at 237–247°. The melting point was 49°. The phenol is quite soluble in the ordinary solvents and crystallizes from 80% alcohol in light yellow needles melting at 50°. Betteridge³ states that the melting point of his *o*-acetyl-*p*-cresol was 50°.

Calcd. for $C_9H_{10}O_2$: C, 72; H, 6.66; found: C, 71.7; H, 7.10.

2-Ethyl-4-methylphenol, VII.—Thirty-seven grams of 2-hydroxy-5-methyl acetophenone were suspended in 300 cc. of hydrochloric acid with 120 g. of zinc-amalgam. The mixture was then boiled 18 hours on a sand bath. The acid solution was extracted with ether, and the ethereal solution of the phenol dried over calcium chloride. After removal of the ether, the phenol was then purified by fractional distillation at ordinary pressure. Fifteen grams of a heavy oil were obtained boiling at 216–218°.

¹ *Ber.*, 33, 2646 (1900).

² *J. prakt. Chem.*, [2] 69, 436 (1904).

³ *Loc. cit.*

The oil was light yellow, but assumed a much darker color on exposure to the air.

Calc. for $C_9H_{10}O$: C, 79.41; H, 8.82; found: C, 79.72; H, 8.76.

Phenyl Urethane of 2-Ethyl-4-methylphenol, $C_6H_5NHCOOC_2H_4(C_2H_5)(CH_3)$.—An intimate mixture of 5 g. of 2-ethyl-4-methylphenol, 2.5 g. of phenyl isocyanate, and a small quantity of aluminium chloride (as a catalyst) were heated for 16 hours in a brine bath. Anhydrous conditions were maintained throughout the heating period by the use of calcium chloride tubes. The semisolid product was finally extracted with ether from the suspended aluminium chloride. After evaporation of the ether, the dark-colored residue was purified by several crystallizations from alcohol. The pure urethane crystallized from this solvent in colorless square plates, which melted at 101° . It was soluble in benzene, alcohol, and ether, but difficultly soluble in petroleum ether. Yield, 2 g.

Calc. for $C_{18}H_{17}O_2N$: N, 5.49; found: N, 5.66, 5.26.

2-Hydroxy-5-methylpropiophenone, VIII.—Sixty-five grams of the methyl ether of *p*-cresol were dissolved in 250 cc. of petroleum ether and 72 g. of aluminium chloride suspended in the solution. The flask was then connected to a return condenser and 55 g. of propionyl chloride slowly added. The solution was heated for 30 hours in a water bath, when the petroleum ether was decanted as in the preparation of 2-hydroxy-5-methyl-acetophenone and the residue disintegrated by pouring into ice-cold hydrochloric acid. After extraction with ether, and drying over calcium chloride the phenol was subjected to distillation under diminished pressure. Twenty-five grams of 2-hydroxy-5-methyl-acetophenone (b. p. 153_{40} —m. p. 2°) were thus obtained. The physical characteristics of this compound agree with those of Betteridge's so-called *o*-propionyl-*p*-cresol. It gave a positive test with Millon's reagent.

2-Propyl-4-methylphenol, IX.—This compound was prepared by the reduction of 2-hydroxy-5-methyl-propiophenone in accordance with the following procedure: Thirty-two grams of 2-hydroxy-5-methyl-propiophenone were digested for 18 hours with 150 g. of zinc-amalgam and 250 cc. of hydrochloric acid. After the usual extraction with ether and drying over calcium chloride, the reduced product was distilled under diminished pressure. The fraction boiling at $128-130_{27}$ analyzed for 2-propyl-4-methylphenol. The phenol is light yellow in color. It showed no tendency to crystallize even upon long standing in a freezing mixture. Yield, 19 g.

Calc. for $C_{10}H_{14}O$: C, 80; H, 9.33; found: C, 79.6; H, 9.21.

This compound was also obtained by the reduction of 2-propenyl-4-methylphenol (XIII). The synthesis of the latter as well as the corresponding 2-allyl-4-methylphenol has been fully described by Claisen.¹

¹ *Loc. cit.*

We were unable to accomplish the reduction of the allyl derivative with any of the following reducing agents:

1. Zinc-amalgam in hydrochloric acid.
2. Hydriodic acid and phosphorus.
3. Sodium or sodium-amalgam in alcohol.

The reduction of 2-propenyl-4-methylphenol was carried out as follows:

Thirty-eight grams of metallic sodium were slowly added to a boiling solution of 33 g. of 2-propenyl-4-methylphenol in 300 cc. of absolute alcohol. After the sodium had completely dissolved, the alcohol was distilled off, and the residue after solution in water was acidified with dilute sulfuric acid. The separated oil was extracted with ether and dried over fused sodium sulfate. Upon distillation under diminished pressure 26 g. of a light yellow oil were obtained boiling at 130° at 25 mm. pressure. This oil analyzed for 2-propyl-4-methylphenol. However, to prove with certainty that it was identical with our previously prepared 2-propyl-4-methylphenol, we converted it into its urethane. We again obtained the urethane of 2-propyl-4-methylphenol, which melted unchanged at 99° with the urethane obtained from the reduction product of 2-hydroxy-5-methyl-propioophenone.

Calc. for $C_{17}H_{19}O_2N$: N, 5.20; found: N, 5.12, 5.09.

Phenylurethane of 2-Propyl-4-methylphenol, $C_6H_5NHCOOC_6H_3(CH_3)_2$

$(CH_3)_2$.—Five grams of 2-propyl-4-methylphenol, 2.5 g. of phenyl isocyanate and 0.2 g. of aluminium chloride were heated for 12 hours under carefully maintained anhydrous conditions. The resulting semi-solid mass was extracted with ether. After evaporation of the ether, a solid remained which was triturated with ligroin to remove resinous matter and then purified by several crystallizations from alcohol. The pure urethane crystallizes in small needles which melt at 99° . It is soluble in alcohol, ether and benzene, but difficultly soluble in ligroin.

Calc. for $C_{17}H_{19}O_2N$: N, 5.20; found: N, 5.38.

Phenylurethane of 2-Allyl-4-methylphenol, $C_6H_5NHCOOC_6H_3(C_2H_5)(CH_3)$

(CH_3) .—This new urethane was prepared by heating an intimate mixture of 2 g. of 2-allyl-4-methylphenol, 1.6 g. of phenyl isocyanate and 0.3 g. of aluminium chloride at 104° for 14 hours. The reaction product was dissolved in hot alcohol. Upon cooling the solution, the urethane separated in thin needles melting at 68° . It is very soluble in alcohol, petroleum ether and benzene. The yield was excellent.

Calc. for $C_{17}H_{17}O_2N$: N, 5.24; found: N, 5.30, 5.28.

3-Ethyl-4-methylaniline, XVII.—Nineteen grams of 3-acetylamido-6-methyl-chloroacetophenone were digested with 70 g. of zinc-amalgam and 300 cc. of hydrochloric acid for 16 hours. After filtering from zinc-

amalgam and mercury, the solution was made distinctly alkaline with ammonium hydroxide and then extracted with ether. This ether solution was dried over sodium sulfate and after removing the ether in the usual manner the base was distilled. Since 2-ethyl-4-methylaniline is not stable, we immediately converted the base into its sulfuric acid salt by solution in equal volumes of dilute sulfuric acid and 50% alcohol. A crystalline product separated upon standing. This product was crystallized twice from dilute alcohol, out of which it separated in characteristic plates melting approximately at 178°. It is soluble in alcohol and ether. Yield, 4 g.

Calc. for $(C_8H_{11}N)_2H_2SO_4$: N, 7.609; found: 7.506, 7.72.

2-Ethyl-4-methylaniline, XIV.—This compound was previously synthesized by Willgerodt and Brandt¹ by the action of molecular quantities of *p*-toluidine, ethyl alcohol and zinc-chloride at 280°. The writers obtained this same amine by the reduction of 2-acetylamido-5-methyl-chloroacetophenone with zinc-amalgam and hydrochloric acid. The procedure followed in this reduction was similar to that employed in the reduction of 3-acetylamido-6-methyl-chloroacetophenone. The product of the reaction was an oil which distilled at 217–220°. Willgerodt and Brandt assign a boiling point of 218–220° to their compound. Owing to the instability of the base, it was converted into its sulfuric acid salt by solution in 50% alcohol and sulfuric acid. The salt soon separated in characteristic platy crystals melting at 241°. The physical and chemical properties of this sulfate are entirely in accord with those of the sulfate described by Willgerodt and Brandt.

Calc. for $(C_8H_{11}N)_2H_2SO_4$: N, 7.608; found: N, 7.60, 7.55.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXI. A NEW SYNTHESIS OF *o*-TYROSINE.²

BY TREAT B. JOHNSON AND WALTER M. SCOTT.

Received June 8, 1915.

It has already been demonstrated that the *hydantoin-method* of synthesizing α -amino acids is one of quite general application. In fact, the results obtained thus far, and discussed in previous papers from this laboratory, show that the methylene radical of the polypeptide grouping— $NH.CH_2.CO$ —in a hydantoin is as reactive towards the aldehyde group as is the same combination in the hippuric acid molecule $C_6H_5CONHCH_2$.

¹ *J. prakt. Chem.*, [2] 69, 436 (1904).

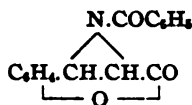
² Part of a dissertation presented by Mr. Walter Moody Scott to the Faculty of the Graduate School of Yale University, 1915, in Candidacy for the Degree of Doctor of Philosophy.

COOH. Twelve aldehydes have thus far been included in our researches, of which every one has interacted smoothly with hydantoin or 2-thiohydantoin with formation of the corresponding condensation products. The choice of aldehydes, however, has purposely been confined to representatives of the aromatic series. The only possible exception is that of cinnamic aldehyde, which may be viewed either as an aromatic or an aliphatic representative. Attempts are now being made to apply our method of α -amino acid synthesis with aliphatic aldehydes. In order to obtain still further evidence of the utility of our method we deemed it desirable, for several reasons, to demonstrate its application for the synthesis of *o*-tyrosine from salicylic aldehyde. This has now been accomplished and likewise the complete synthesis of the methyl ether of *o*-tyrosine from methyl salicylic aldehyde. A complete description of these two syntheses is now recorded in this paper.

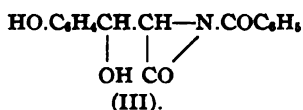
That salicylic aldehyde will condense with hippuric acid in the presence of acetic anhydride was first observed by Plöchl and Wolfrum.¹ They represented the condensation product as an anhydride, corresponding to Formula I, which was converted on hydrolysis into a benzoylimido-cumarin represented by Formula II. Rebuffat² later applied the same reaction and apparently obtained the same products as described by Plöchl and Wolfrum. He assigned, however, to his primary condensation product the structural formula III. Both of these interpretations were,



(I).



(II).



(III).

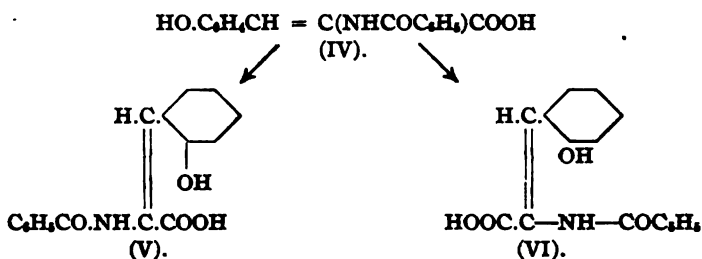
however, shown to be incorrect. The true explanation of the nature of these aldehyde condensation products was given by Erlenmeyer, Jr., in a series of papers published several years later.³ Erlenmeyer and Stadlin⁴ showed that salicylic aldehyde, for example, condenses normally with hippuric acid giving first the unsaturated acid IV, which they assumed was capable of existing in two stereoisomeric modifications as represented by Formulas V and VI. In the presence of the acetic anhydride these two acids then underwent further characteristic changes. The acid (V)

¹ *Ber.*, 18, 1183 (1885).

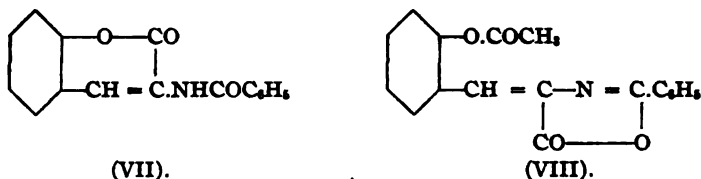
² *Gaz.*, 19, 43 (1889).

³ *Ann.*, 271, 137 (1892); 275, 1 (1893); Erlenmeyer and Stadlin, *Ibid.*, 237, 265, 283; Erlenmeyer and Arbenz, *Ibid.*, 337, 302 (1904).

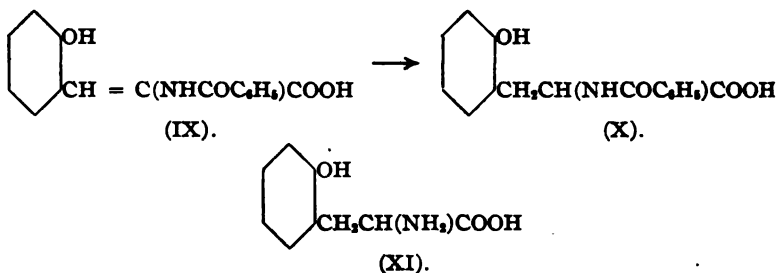
⁴ *Loc. cit.*



was transformed into a colorless benzoylaminocumarin (VII), which was identical with Plöchl and Wolfrum's *benzoylimidocumarin*, while its stereoisomer (VI) underwent acetylation and finally an inner condensation, giving the azlactimide corresponding to Formula VIII.



In 1908, Blum¹ repeated this work of Erlenmeyer and Stadlin's and converted the azlactimide (VIII), by hydrolysis with alkali, into the acrylic acid (IX). The latter, on reduction with sodium amalgam, was then transformed into the acid (X), which was converted into *o*-tyrosine



(XI), by hydrolysis with hydrochloric acid. This is the only method of synthesizing this acid, which has hitherto been described in the literature.

The starting point in our synthesis of *o*-tyrosine was 2-thiohydantoin $\text{NH.CS.NH.CH}_2\text{CO}$, which is now an easily obtainable reagent if glycocholl

is available. If glycocholl is not available any acyl derivative of this amino acid, as hippuric acid, will serve for its preparation. Several hundred grams of the reagent have been prepared in this laboratory during the progress of our hydantoin researches. This thiohydantoin was selected for our investigation after we had made the observation that hydantoin does not react smoothly with salicylic aldehyde to give the corre-

¹ Arch. Exp. Pathol. u. Pharm., 59, 273 (1908).

sponding condensation product, namely, hydroxybenzalhydantoin (XV). On the other hand, 2-thiohydantoin and salicylic aldehyde interact smoothly, when heated together in acetic acid solution and in the presence of fused sodium acetate, giving an excellent yield of the 2-thio-4-hydroxybenzalhydantoin (XVI). The hydantoin (XV), which theoretically should be formed by condensation of hydantoin with salicylic aldehyde, is obtained in almost a quantitative yield by desulfurization of this thiohydantoin (XVI), by digesting with chloroacetic acid.

The thiohydantoin (XVI) undergoes reduction normally by the action of sodium amalgam in an alkaline solution, forming the corresponding saturated derivative—2-thio-4-hydroxybenzylhydantoin (XIV). When the latter compound was digested with chloroacetic acid it was converted smoothly into the hydantoin of *o*-tyrosine (XIII). This same hydantoin (XIII) is also found by reducing the hydroxybenzalhydantoin (XV) with sodium amalgam. In fact, we found that the best method for preparing this hydantoin (XIII) in quantity is to first desulfurize the original thiohydantoin (XVI) with formation of the hydantoin (XV) and then to subject this to reduction with sodium amalgam. By proceeding in the reverse manner, namely, by reduction to the hydantoin (XIV) and then desulfurizing this with chloroacetic acid, a much poorer yield is obtained. By long digestion of the hydantoin (XIII) with an excess of barium-hydroxide solution a good yield of *o*-tyrosine is obtained with evolution of ammonia and formation of barium carbonate. A description of the properties of this acid is given in the experimental part of this paper.

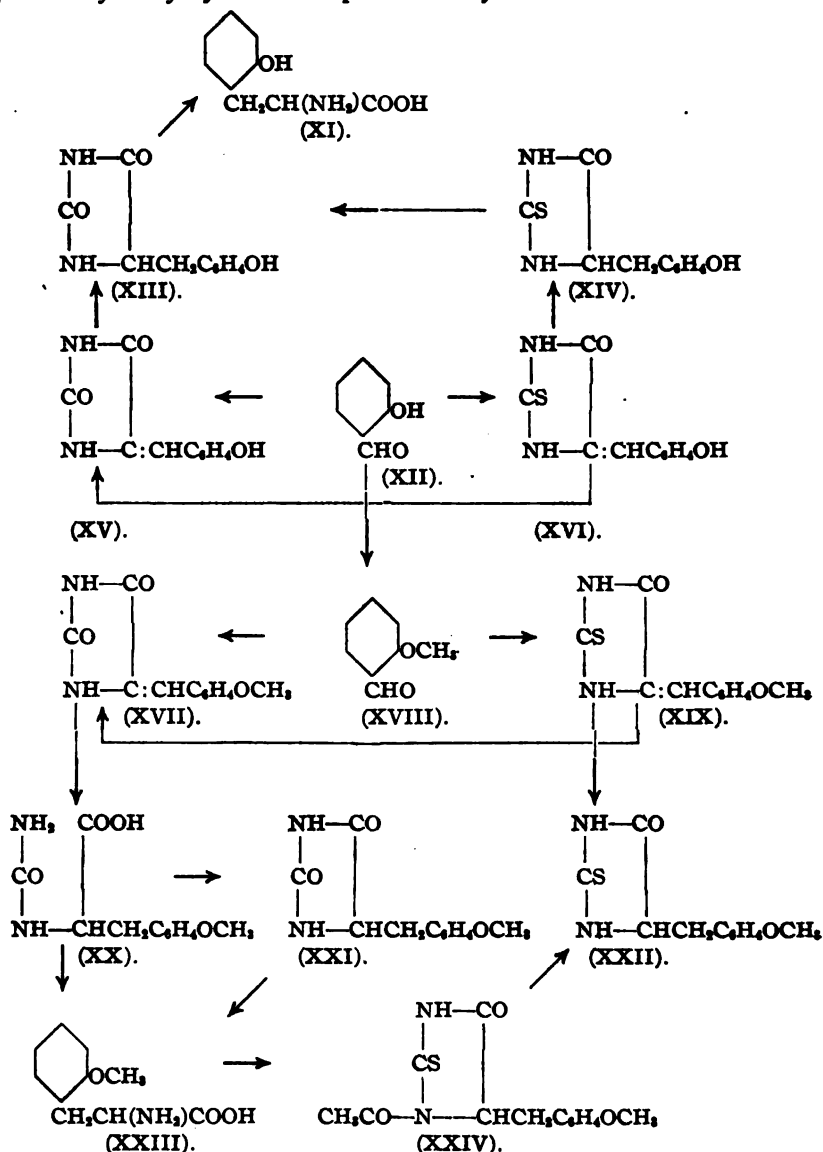
In order to synthesize the methyl ether of *o*-tyrosine (XXIII) we first prepared the methyl ether of salicylic aldehyde according to the method of Voswinckel.¹ Here again we made the observation that 2-thiohydantoin showed a greater tendency to interact with this aldehyde than did plain hydantoin. The condensation product (XVII) could be obtained by interaction of the aldehyde and hydantoin, but the yield was small. On the other hand, 2-thiohydantoin and methylsalicylic aldehyde combined to give an excellent yield of 2-thio-4-methoxybenzalhydantoin (XIX). This hydantoin is easily converted into the hydantoin (XVII) when digested with chloroacetic acid.

While 2-thio-4-methoxybenzalhydantoin (XIX) undergoes reduction with sodium amalgam, in the usual manner, forming the hydantoin (XXII), on the other hand, the hydantoin (XVII) is reduced abnormally by the same reagent, giving the hydantoic acid (XX). This new acid is converted smoothly into the normal hydantoin (XXI), by digesting with concentrated hydrochloric acid. The *o*-methoxyphenylalanine (XXIII) is easily obtained by hydrolysis of the hydantoin (XXI) or its corresponding

¹ Ber., 15, 2024 (1882).

acid (XX) with barium hydroxide. A description of this acid is given in the experimental part of this paper.

Johnson and Nicolet's¹ thiohydantoin reaction can be applied successfully with this amino acid. It reacted normally with ammonium thiocyanate in acetic anhydride solution, giving smoothly the 2-thio-3-acetyl-4-methoxybenzylhydantoin represented by Formula XXIV. When this



¹ THIS JOURNAL, 33, 1973 (1911).

was warmed with hydrochloric acid it underwent hydrolysis with formation of 2-thio-4-methoxybenzylhydantoin (XXII). The various changes involved in the synthesis of these two α -amino acids are represented by the preceding structural formulas.

Our researches on hydantoins will be continued.

Experimental Part.

The 2-thiohydantoin, which was used in this investigation, was prepared according to the method of Johnson and Nicolet¹, namely: by the action of ammonium thiocyanate on hippuric acid in the presence of acetic anhydride.

2-Thio-4-o-hydroxybenzalhydantoin (XVI).—This hydantoin is obtained in nearly a quantitative yield by condensing salicylic aldehyde (XII) with 2-thiohydantoin. Thirty grams of the hydantoin, 37.5 g. of salicylic aldehyde, 90 g. of fused sodium acetate and 230 cc. of glacial acetic acid were heated together in an oil bath for 4 hours at 140–150°. While the reaction mixture was still hot, it was then poured into a large volume of cold water, whereupon the above hydantoin separated immediately. After complete disintegration, to remove sodium acetate, the crude hydantoin was then separated by filtration and purified by crystallization from hot, glacial acetic acid. It separated from this solvent, on cooling, in small clusters of radiating needles which melted at 248°.

Calc. for $C_{10}H_8O_3N_2S$: N, 12.72. Found: N, 12.86, 12.60.

Desulfurization of 2-Thio-4-o-hydroxybenzalhydantoin with Formation of 4-o-Hydroxybenzalhydantoin (XV).—Fifty grams of the thiohydantoin, 150 g. of monochloroacetic acid and 400 cc. of water were placed in a flask and the mixture then digested in an oil bath for 2 hours at 140–150°. Owing to the insolubility of both the thio- and oxyhydantoins a clear solution was never obtained. However, even under such conditions the sulfur was displaced smoothly and an 80% yield of the hydantoin was obtained. After the reaction was complete the benzalhydantoin was separated by filtration, washed thoroughly with water and then purified by crystallization from a large volume of alcohol. It was difficultly soluble in this solvent and separated, on cooling, in the form of short needles which melted at 271° with decomposition.

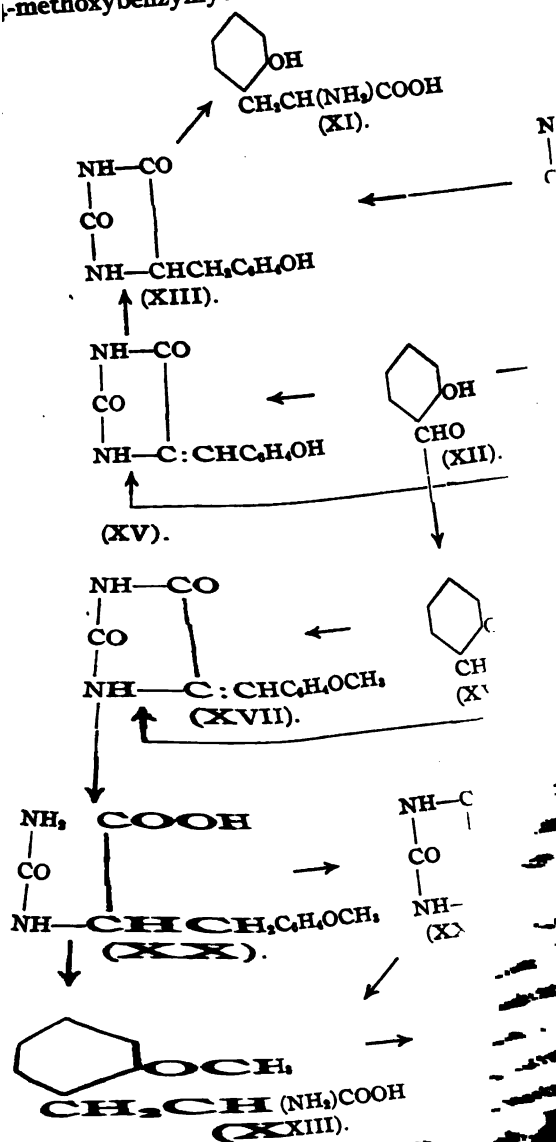
Calc. for $C_{10}H_8O_3N_2$: N, 13.72. Found: N, 13.57, 13.87.

Attempts were made to prepare this new hydantoin directly by condensing salicylic aldehyde with hydantoin. The reaction was applied by digesting the reagents in acetic acid solution in the presence of anhydrous sodium acetate and also in the presence of acetic anhydride. In no case, however, did we observe a smooth formation of the hydantoin. This marked difference in reactivity of hydantoin and thiohydantoin has

¹ *Loc. cit.*

id (XX) with barium hydroxide. A description of the experimental part of this paper.

Johnson and Nicolet's¹ thiohydantoin reaction can ally with this amino acid. It reacted normally with cyanate in acetic anhydride solution, giving smooth methoxybenzylhydantoin represented by Formu



¹ This Journal, 33--

with
conditional
until the crude
the supernatant
hydantoin was obtained
compound was obtained
water. By repeated
was finally obtained.
which melted at 107° to

Found: N, 12.40.

4-methoxybenzylhydantoin with Formic

This change is easily effected by
chloroacetic acid. Three and five
were suspended in 10 cc. of water
acid. After heating this mixture
at 100° , a clear solution was obtained.
crystallization of tyrosine separated in a crystal-
lized by crystallization from water,
crystals which melted at

Found: N, 13.56.

is also formed by reduction of 4-ortho-
with sodium amalgam. In fact, this
the synthesis of this compound. The
Ten grams of the unsaturated
of 30 cc. of 10% sodium hydroxide
solution is then warmed to about 80°
addition of 100 g. of 3% sodium amal-
shy 200 g. more of the amalgam

Practically a colorless solution
 the mercury and acidi-
 orally no precipi-
 on, however,
 addition. It
 d.
 Hydroxide, *o*-

conversion into
 lantoin with strong
 king with 7 g. of the
 ysis was complete after
 no acid the barium was
 e colorless solution of the
 e *o*-tyrosine then separated
 lves with difficulty in water
 only on long standing. Our
 water and then allow the solu-
 vacuum over concentrated sul-
 as obtained nearly colorless and in
 gave Millon's test and also a violet
 allowed to interact with ferric chloride.
 d a melting point of 249-250°. It was
 is an indefinite decomposition point. If
 it underwent a noticeable change at about
 rvescence and forming an oil which solidi-
 stance did not undergo further change until
 h was raised to 270° when it finally melted to
 e of primary decomposition was indefinite de-
 heating. If heated rapidly there was no evidence
 out the substance decomposed at 247-250°. It is
 sine undergoes an inner condensation on melting
 cule of water.

for $C_9H_{11}O_2N$: N, 7.73. Found: N, 7.72.

of *o*-Tyrosine.—Crystallizes from dilute hydrochloric
 ic crystals which decompose at 180°.

Calc. for $C_9H_{11}O_2NCl$: N, 6.44. Found: N, 6.39, 6.53.

salicylic aldehyde (XVIII) which was used in the following
 prepared according to the directions of Voswinckel¹ by alkylation
 aldehyde (XII) with methyl iodide in the presence of sodium

te.

oil.

From 20 g. of salicylic aldehyde we obtained 17.5 g. of its methyl ether boiling at 236–240°. Voswinckel assigned to the oil a boiling point of 238°.

Condensation of Methylsalicylic Aldehyde with 2-Thiohydantoin.

2-Thio-4-*o*-methoxybenzalhydantoin (XIX).—The following proportions were taken for the preparation of this compound: 10.3 g. of thiohydantoin, 12 g. of the aldehyde, 30 g. of fused sodium acetate and 75 cc. of glacial acetic acid. This mixture was then heated in an oil bath at 140–150° for 6 hours, when it was poured while warm into a large volume of cold water. The thiohydantoin separated at once in a crystalline condition. The yield was 20.5 g. which was almost equal to the theoretical amount. The hydantoin was purified by crystallization from alcohol and melted at 227° to an oil. It crystallized in the form of needles.

Calc. for $C_{11}H_{10}O_2N_2S$: N, 11.96. Found: N, 11.82, 11.91.

Condensation of Methylsalicylic Aldehyde with Hydantoin.

4-*o*-Methoxybenzalhydantoin (XVII).—The following proportions were taken for the preparation of this hydantoin: 2.5 g. of hydantoin, 3.5 g. of the aldehyde, 7.5 g. of sodium acetate and 25 cc. of glacial acetic acid. This mixture was then heated at 130–140° for 4 hours when a clear solution was obtained, which solidified on cooling. This product was then dissolved in a small volume of hot water and the solution cooled when the above hydantoin separated. The yield was only 2.2 g. It was purified by crystallization from alcohol and melted at 178°.

A 75% yield of this same hydantoin is obtained by desulfurization of 2-thio-4-*o*-methoxybenzalhydantoin (XIX). Eight grams of the thiohydantoin were digested with 16.3 g. of chloroacetic acid and 50 cc. of water for 4 hours at 130–140°. A clear solution was obtained from which the above hydantoin immediately separated on cooling. It crystallized from 95% alcohol in long, slender prisms or needles which melted at 178° to an oil.

Calc. for $C_{11}H_{10}O_2N_2$: N, 12.84. Found: N, 12.81, 12.91.

Reduction of 4-*o*-Methoxybenzalhydantoin with Sodium Amalgam.

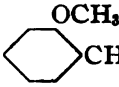
***o*-Methoxybenzylhydantoic Acid (XX).**—One hundred and seventy-five cubic centimeters of a 10% solution of sodium hydroxide were mixed with 300 cc. of water and 30 g. of the above hydantoin dissolved in the solution with the aid of heat. If this solution was cooled after complete solution of the hydantoin its sodium salt separated immediately in colorless crystals. In order to keep this salt in solution the latter was heated to 80–90° and then 600 g. of 3% amalgam slowly added. After the final addition of amalgam the solution was then warmed for 3–4 hours and finally acidified with dilute hydrochloric acid. There was an immediate precipitation of the hydantoic acid. The yield was 29 g. This new acid

crystallized from alcohol in rectangular prisms which melted at 189° with effervescence.

Calc. for $C_{11}H_{14}O_4N_2$: N, 11.76. Found: N, 11.87, 11.64.

4-*o*-Methoxybenzylhydantoin (XXI).—The 29 g. of the hydantoic acid from the preceding experiment were converted into this hydantoin by warming with dilute hydrochloric acid. The hydantoic acid dissolved in this solvent on warming, but as the heating was continued the hydantoin finally deposited from the hot solution. The hydantoin is practically insoluble in cold hydrochloric acid. It is easily purified by crystallization from alcohol and separates from this solvent in prisms which melt at 186° to an oil. The yield was quantitative.

Calc. for $C_{11}H_{14}O_4N_2$: N, 12.73. Found: N, 12.57, 12.68.

***o*-Methoxyphenylalanine,**  **CH₂.CH(NH₂).COOH.**—This amino acid is easily obtained by hydrolysis of the above hydantoic acid or the hydantoin (XXI), with strong barium hydroxide solution. Our procedure was practically the same as that applied in the preparation of *o*-tyrosine from its hydantoin. From 7.5 g. of the hydantoic acid we obtained 4 g. of the α -amino acid. It was purified by crystallization from hot water and separated in rosettes of needles. The acid melted at 206° with effervescence.

Calc. for $C_{10}H_{12}O_3N$: N, 7.18. Found: N, 7.21, 7.14.

Condensation of *o*-Methoxyphenylalanine with Ammonium Thiocyanate in Acetic Anhydride Solution.

2-Thio-3-acetyl-4-*o*-methoxybenzylhydantoin (XXIV).—This hydantoin is easily obtained by warming 1.5 g. of the α -amino acid and 0.7 g. of dry ammonium thiocyanate with 8 cc. of acetic anhydride and 1 cc. of glacial acetic acid for 30 minutes at 100° . On pouring the resulting solution into water the hydantoin separated immediately. The yield was excellent. The hydantoin was purified by crystallization from alcohol and melted at 168° .

Calc. for $C_{13}H_{14}O_3N_2S$: N, 10.07. Found: N, 10.05.

2-Thio-4-*o*-methoxybenzylhydantoin (XXII).—A quantitative yield of this compound was obtained by hydrolysis of the preceding hydantoin with hydrochloric acid. It was purified for analysis by crystallization from alcohol and melted at 190° .

This same 2-thiohydantoin was also obtained by reduction of the above 2-thio-4-*o*-methoxybenzalhydantoin (XIX) with sodium amalgam. This was accomplished by dissolving 5 g. of the thiohydantoin in dilute alkali and then reducing with 100 g. of sodium amalgam at 70 – 80° . When the reduction was complete the solution was then acidified with hydrochloric acid when an oil separated which soon solidified. This substance

was then warmed with an excess of hydrochloric acid to convert any hydantoic acid present into hydantoin and then finally purified by crystallization from alcohol. It melted at 190°.

Calc. for $C_{11}H_{12}O_2N_2S$: N, 11.86. Found: N, 11.80.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXII. SYNTHESIS OF THE HYDANTOIN OF 2-HYDROXY-5-AMINOPHENYLALANINE.¹

BY TREAT B. JOHNSON AND WALTER M. SCOTT.

Received June 11, 1915.

The hydantoins of aminophenylalanine derivatives have become of especial interest to us because it now seems very probable that they will find application for the synthesis of α -amino acids of biochemical interest, which it is now practically impossible to prepare easily by other methods. They should be valuable for operations where it is desired to introduce groups into the benzene nucleus by application of the diazo reaction, because the basic influence of the α -amino group of the acid is completely neutralized in such combinations. Furthermore, it has been our experience that the incorporation of the hydantoin nucleus tends to bestow physical properties which are very essential for synthetical work. Such cyclic combinations should be especially valuable for developing methods of synthesizing new, isomeric halogen derivatives of phenylalanine and tyrosine. The iodine derivatives of these two acids are of special physiological interest at the present time. Investigations dealing with methods of synthesis, and other phases of these interesting problems are now in progress in this laboratory.

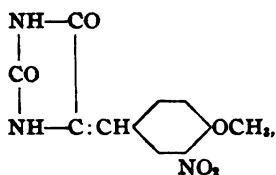
The only aminohydantoin derivatives of phenylalanine or tyrosine which have hitherto been available for synthetical work are the hydantoins of 3-aminotyrosine (III), and its corresponding methyl ether (II), which have been described by Johnson and Bengis² in a previous paper from this laboratory. They were prepared by the reduction of 3-nitro-4-methoxybenzalhydantoin (I) with hydriodic acid, and tin and hydrochloric acid, respectively. Johnson and Bengis employed the hydantoin (II), for the synthesis of monobromotyrosine (V).³ This was accomplished by diazotization of the amino group and by subsequent introduction of bromine into the benzene ring in the usual manner. On subjecting the resulting bromohydantoin to hydrolysis 3-bromo-4-methoxyphenyl-

¹ Part of a dissertation presented by Mr. Walter M. Scott to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

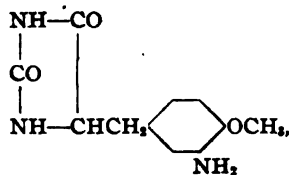
² THIS JOURNAL, 34, 1054 (1912).

³ *Ibid.*, 34, 1061 (1912).

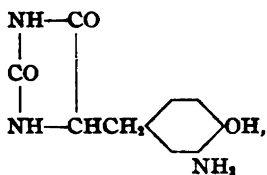
alanine (IV) was formed. This was then converted into monobromotyrosine (V) by warming with hydriodic acid.



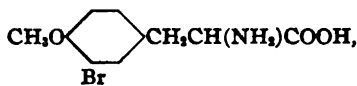
(I).



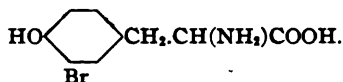
(II).



(III).



(IV).



(V).

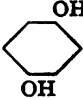
Isomeric with the hydantoin of aminotyrosine (III), is the hydantoin of 2-hydroxy-5-aminophenylalanine which is represented by Formula XIV, and which was unknown at the time we began our investigation. The starting point for its synthesis was 2-hydroxy-5-nitrobenzaldehyde (VII), which was prepared according to the method described by Miller,¹ namely, by nitration of salicylic aldehyde (VI). The isomeric 2-hydroxy-3-nitrobenzaldehyde, which is also one of the products of this reaction, will be of value for further syntheses. When this nitroaldehyde (VII) was digested with 2-thiohydantoin in acetic acid solution and in the presence of sodium acetate, a normal condensation was easily effected and practically a quantitative yield of 2-thio-4-(2-hydroxy-5-nitrobenzal)-hydantoin (VIII) was obtained. By heating this thio compound with chloroacetic acid in aqueous solution the sulfur was quantitatively replaced by oxygen and the corresponding hydantoin represented by Formula XI was formed. The last step in the synthesis was accomplished by digestion of the nitrohydantoin (XI) with tin and hydrochloric acid. The reduction proceeded normally and after removal of the tin the aminohydantoin (XIV) was isolated in the form of its hydrochloric acid salt. When this hydrochloride was treated in aqueous solution with the required amount of sodium nitrite it was transformed normally into its diazonium derivative. This separated in a crystalline condition and was insoluble in cold water. On warming with water, however, nitrogen was evolved and an excellent

¹ Ber., 20, 1928 (1886).

yield of the hydantoin of 2,5-dihydroxyphenylalanine (XVII) was obtained.

The α -amino acid-2,5-dihydroxyphenylalanine (hydrochinonalanine) (XVI) has never been synthesized, and if known would undoubtedly be an unstable substance. Especial biochemical interest attaches to this compound, however, due to the possibility of its actually functioning as an intermediate product in the formation of homogentisic acid from tyrosine and phenylalanine in cases of alcaptonuria. In fact, Neubauer first gave expression to the possibility of such an intermediate acid being involved in such transformations, when, in his paper entitled—"Über den Abbau der Aminosäuren im gesunden und kranken Organismus," he wrote as follows:¹

"— es würde da das Phenylalan in zunächst in gewöhnliches *p*-Tyrosin übergehen; es wäre möglich, dass dann sofort die Chinonbildung und die Umlagerung in das Hydrochinonderivat stattfindet; jedenfalls wäre es von Interesse, das noch unbekannte Hydro-

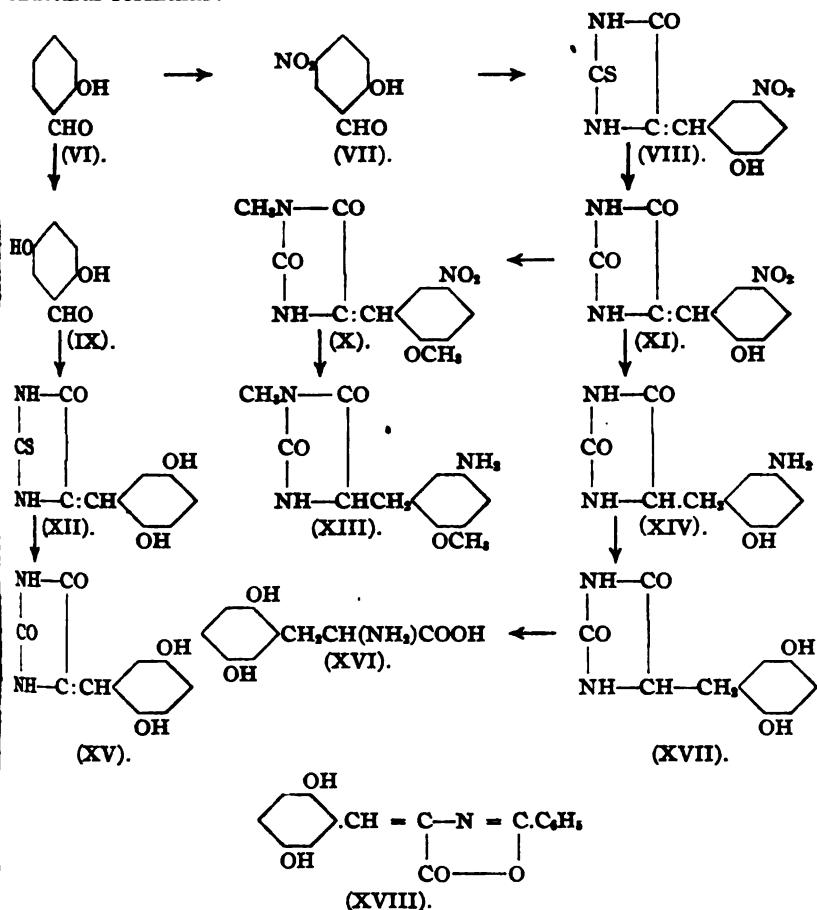
chinonalanin  $\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, das dabei entstehen müsste, auf sein Verhalten beim Alkaptonuriker zu untersuchen."

Attempts to prepare this α -amino acid (XVI) from its corresponding hydantoin (XVII) have so far been unsuccessful. The hydantoin (XVII) is extremely unstable and it was practically impossible to obtain it in a colorless condition. It was subjected to hydrolysis with barium hydroxide and also sulfuric acid under pressure, but, by both procedures, we obtained only an amorphous product possessing indefinite properties. The substance obtained gave Millon's reaction, but no definite combinations with picric or picrolonic acids, mercury chloride or platinum chloride could be obtained, which would justify a conclusion that we were dealing with a definite compound. It now appears from our experience with the hydantoin that the most feasible way of preparing the amino acid (XVI) will be to synthesize its corresponding dimethyl ether, which should be a stable compound, and then convert this into the amino acid by demethylation under special conditions. Further work on this problem is now in progress.

In connection with our work on methods of preparing the hydantoins of 2,5-dihydroxyphenylalanine (XVII), we also investigated the action of gentisinic aldehyde (IX) on 2-thiohydantoin. These reagents interacted normally when heated together in acetic acid solution and in the presence of sodium acetate, giving the corresponding condensation product represented by Formula XII. On digesting this with chloroacetic acid in aqueous solution it was converted smoothly into the hydantoin (XV). This was a very insoluble compound and possessed no definite melting

¹ *Deutsch. Archiv. f. Klin. Med.*, 95, 211 (1908).

point. An attempt to convert it into the hydantoin (XVII) by reduction with sodium amalgam was unsuccessful because of its great instability in alkaline solution. The azolactone (XVIII) obtained by condensing gentisinic aldehyde (IX) with hippuric acid was also observed by Neubauer and Flatow¹ to be an extremely unstable compound. The various changes discussed in the previous pages are represented by the following structural formulas:



Experimental Part.

Condensation of Gentisinic Aldehyde (IX) with 2-Thiohydantoin.

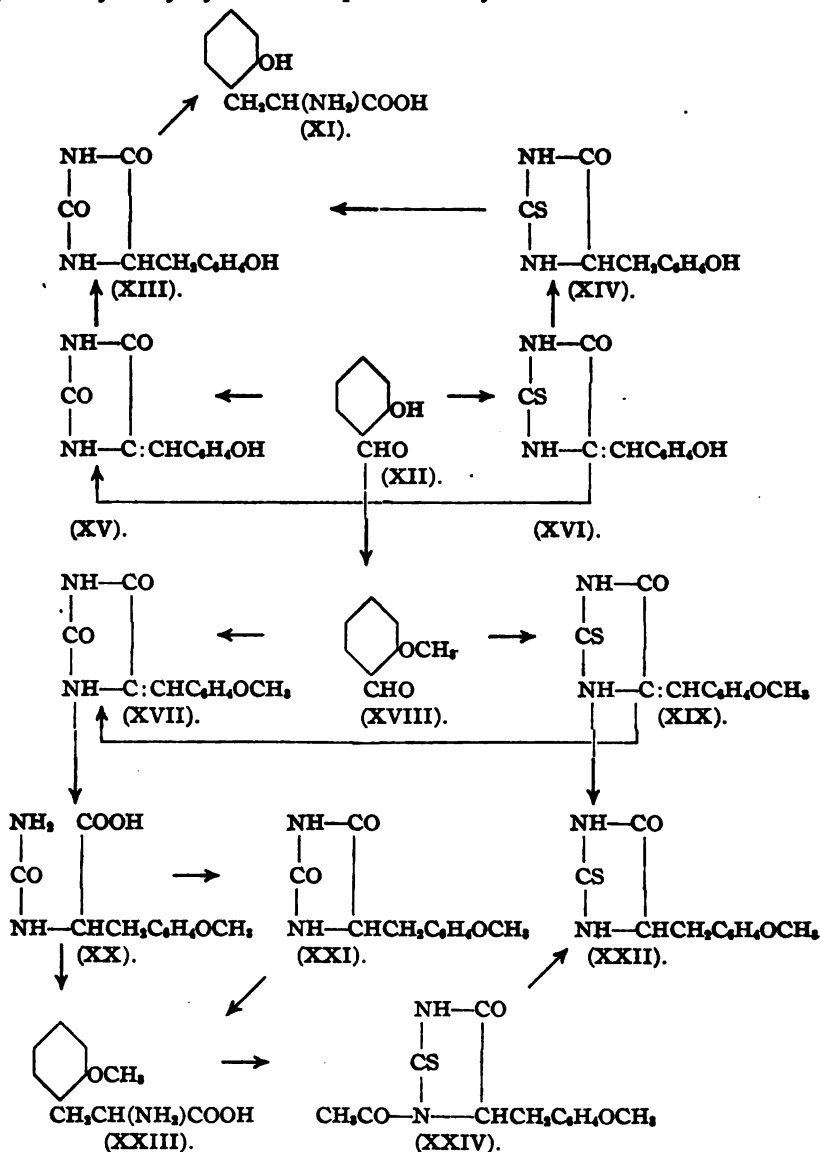
2-Thio-4-(2,5-dihydroxybenzal)-hydantoin (XII).—The gentisinic aldehyde, which was used in this work, was prepared by oxidation of salicylic aldehyde. Neubauer and Flatow² accomplished this change

¹ *Z. physiol. Chem.*, **52**, 383 (1907).

² *Loc. cit.*

acid (XX) with barium hydroxide. A description of this acid is given in the experimental part of this paper.

Johnson and Nicolet's¹ thiohydantoin reaction can be applied successfully with this amino acid. It reacted normally with ammonium thiocyanate in acetic anhydride solution, giving smoothly the 2-thio-3-acetyl-4-methoxybenzylhydantoin represented by Formula XXIV. When this



¹ THIS JOURNAL, 33, 1973 (1911).

was warmed with hydrochloric acid it underwent hydrolysis with formation of 2-thio-4-methoxybenzylhydantoin (XXII). The various changes involved in the synthesis of these two α -amino acids are represented by the preceding structural formulas.

Our researches on hydantoin will be continued.

Experimental Part.

The 2-thiohydantoin, which was used in this investigation, was prepared according to the method of Johnson and Nicolet¹, namely: by the action of ammonium thiocyanate on hippuric acid in the presence of acetic anhydride.

2-Thio-4-o-hydroxybenzalhydantoin (XVI).—This hydantoin is obtained in nearly a quantitative yield by condensing salicylic aldehyde (XII) with 2-thiohydantoin. Thirty grams of the hydantoin, 37.5 g. of salicylic aldehyde, 90 g. of fused sodium acetate and 230 cc. of glacial acetic acid were heated together in an oil bath for 4 hours at 140–150°. While the reaction mixture was still hot, it was then poured into a large volume of cold water, whereupon the above hydantoin separated immediately. After complete disintegration, to remove sodium acetate, the crude hydantoin was then separated by filtration and purified by crystallization from hot, glacial acetic acid. It separated from this solvent, on cooling, in small clusters of radiating needles which melted at 248°.

Calc. for $C_{10}H_8O_2N_2S$: N, 12.72. Found: N, 12.86, 12.60.

Desulfurization of 2-Thio-4-o-hydroxybenzalhydantoin with Formation of 4-o-Hydroxybenzalhydantoin (XV).—Fifty grams of the thiohydantoin, 150 g. of monochloroacetic acid and 400 cc. of water were placed in a flask and the mixture then digested in an oil bath for 2 hours at 140–150°. Owing to the insolubility of both the thio- and oxyhydantoin a clear solution was never obtained. However, even under such conditions the sulfur was displaced smoothly and an 80% yield of the hydantoin was obtained. After the reaction was complete the benzalhydantoin was separated by filtration, washed thoroughly with water and then purified by crystallization from a large volume of alcohol. It was difficultly soluble in this solvent and separated, on cooling, in the form of short needles which melted at 271° with decomposition.

Calc. for $C_{10}H_8O_2N_2$: N, 13.72. Found: N, 13.57, 13.87.

Attempts were made to prepare this new hydantoin directly by condensing salicylic aldehyde with hydantoin. The reaction was applied by digesting the reagents in acetic acid solution in the presence of anhydrous sodium acetate and also in the presence of acetic anhydride. In no case, however, did we observe a smooth formation of the hydantoin. This marked difference in reactivity of hydantoin and thiohydantoin has

¹ Loc. cit.

This compound gradually underwent oxidation and dissolved in sodium hydroxide forming a dark-colored solution. It dissolved in both hydrochloric and sulfuric acids giving characteristic, purple solutions. The hydantoin was insoluble in alcohol and was finally prepared for analysis by digesting with alcohol to remove impurities. It did not possess a sharp melting point, but turned dark colored on heating and underwent partial decomposition at about 170° but did not melt below 290° . The yield was 10 g.

Calc. for $C_{10}H_{10}O_4N_2$: N, 12.61. Found: N, 12.34.

Behavior of 4-(2,5-Dihydroxybenzyl)-hydantoin when Heated with Barium Hydroxide and Sulfuric Acid.—Our attempts to obtain 2,5-dihydroxyphenylalanine (XVI) from this hydantoin were unsuccessful. The hydantoin is extremely unstable in alkaline and also acid solutions, apparently undergoing oxidation and hydrolysis under both conditions to a dark-colored, amorphous product. For example, in one experiment 2 g. of the hydantoin were digested with 15 g. of barium hydroxide in 75 cc. of water for several days or until the evolution of ammonia had ceased. The barium was then quantitatively removed by precipitation as barium sulfate when we obtained a brown-colored solution containing apparently the desired amino acid. On concentrating this solution, however, it gradually grew darker in color, finally becoming almost black. After complete evaporation a dark brown residue was obtained which was amorphous in character and possessed no definite melting point. The substance contained nitrogen but the analytical values obtained did not indicate that we were dealing here with a definite compound.

We also heated the hydantoin with 30% sulfuric acid at 160° for 6 hours. It was completely decomposed by this treatment with formation of ammonium sulfate. Much black insoluble material was also suspended in the solution when the pressure tube was examined. The acid solution was filtered and the sulfuric acid completely precipitated as barium sulfate. After filtering off the barium sulfate a clear solution was obtained indicating the possibility of isolating here the amino acid. The solution was divided into two equal portions and one acidified with dilute hydrochloric acid. On evaporating, both gradually assumed a dark color owing to oxidation and in both cases only dark-colored, indefinite residues were obtained. The product obtained by evaporation of the aqueous solution gave a positive test with Millon's reagent, but did not give a violet-colored solution when dissolved in a solution of ferric chloride. No precipitates were obtained by adding picric acid, picrolonic and phosphotungstic acids to an aqueous solution of the hydrolytic product. Mixed with the residue obtained by evaporation of the hydrochloric acid solution, was a small amount of ammonium chloride.

1-Methyl-4-(2-methoxy-5-nitrobenzal)-hydantoin (X).—Two grams of sodium were dissolved in 50 cc. of methyl alcohol, and 5 g. of 4-(2-hydroxy-5-nitrobenzal)-hydantoin (XI) and 10 g. of methyl iodide added to the cold sodium methylate solution. This mixture was then heated in a pressure bottle for 6 hours at 100° when a clear solution was obtained. The alcohol was then evaporated and the residue left behind dissolved in a small volume of dilute sodium hydroxide solution. On acidifying the warm solution, and finally cooling this hydantoin separated immediately. It was purified by crystallization from dilute acetic acid and melted at 265° with effervescence. The yield was 6 g.

Calc. for $C_{12}H_{11}O_4N_3$: N, 15.16. Found: N, 15.11.

Reduction of the Nitrohydantoin (X) with Tin and Hydrochloric Acid.

Hydrochloride of 1-Methyl-4-(2-methoxy-5-aminobenzyl)-hydantoin (XIII).—The reduction was applied under practically the same conditions as described in the preparation of 4-(2-hydroxy-5-aminobenzyl)-hydantoin (see above). In this case the hydrochloride was extremely soluble in water. It separated from this solvent as a light-colored, crystalline powder, which possessed no definite melting point but gradually decomposed when heated above 175°. It did not give a red color with Millon's reagent.

Calc. for $C_{12}H_{13}O_3N_2Cl$: N, 14.76. Found: N, 14.67.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

STUDIES ON NITRATED PROTEINS: I. THE DETERMINATION OF THE STRUCTURE OF NITROTYROSINE.¹

BY TRENT B. JOHNSON AND EDWARD F. KOHMANN.

Received June 11, 1915.

Introduction.

This paper is the first of a projected series of publications from this laboratory, dealing with the chemistry of nitrated proteins. A short, historical review of work already done in this field, previous to the inception of our investigations, has been incorporated. We do not claim to have included here references to all the work done and it is quite probable that some papers have been overlooked. Many of the older journals have been inaccessible to us and consequently we have been obliged to acquire our information regarding some of the earlier developments from the abstract journals. These sources of information are not always reliable. The results obtained in our new researches will be discussed in proper order in subsequent papers. These will have to deal with new data contributing to the present knowledge of the Xanthoproteic and

¹ Part of a dissertation presented by Mr. Edward F. Kohmann to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the degree of Doctor of Philosophy.

Millon's reactions, and also with the study of new organic combinations obtained by hydrolysis of nitrated proteins.

Historical.

I. Definite Nitro-compounds which have been Obtained by Vigorous Treatment of Proteins with Nitric Acid.—While it has been known for a long time that nitric acid will act upon animal and vegetable proteins with production of a yellow color, the study of the reactions involved can be said to have begun, apparently, in the year 1771, when Woulfe¹ made the observation that natural indigo interacts with nitric acid, giving an aqueous solution which will dye silk yellow. Haussmann² repeated his work in 1788 and succeeded in isolating a crystalline substance whose constitution was not established. Welter³ was apparently the first to study the action of nitric acid on protein and obtained, by treatment of silk with nitric acid, a characteristic substance which he called "Amer." He observed that all animal substances, which he examined, were stained yellow by nitric acid. Welter's observations were confirmed by Fourcroy and Vanquelin,⁴ who were apparently the first to venture an expression of the constitution of Amer with the following phrase: "hydrocarbure d'azote suroxigène." Hatschett⁵ also investigated the action of nitric acid on proteins and later Chevreul,⁶ in 1809, supplemented his work and made a thorough study of "Amer." In 1828 Liebig⁷ continued the investigation of previous investigators and prepared again Welter's Amer. He named it "Kohlenstickstoff," and gave precise directions for its preparation. Berzelius⁸ designated it as "Pikrinsalpetersäure," while its present name—picric acid—was assigned to it, in 1841, by Dumas.⁹ Its constitution was finally established by Laurent¹⁰ in 1842. A second nitro-compound—*p*-nitrobenzoic acid—was obtained, in 1885, by Nencki and Sieber¹¹ by the action of nitric acid on globin, casein and albumin. As far as the writers are aware, this acid and trinitrophenol (picric acid) are the only two nitro-compounds of known structure which have been obtained by nitration and hydrolysis of proteins with nitric acid.

II. Nitroproteins Formed by Interaction of Nitric Acid with Proteins, and the Nitro-compounds of Definite Constitution, which have been Ob-

¹ *Phil. Trans.*, 1771.

² *J. Phys. Chim.*, 32, 161.

³ *Ann. chim.*, 29, 301.

⁴ *J. Chem. Physik.*, 2, 231.

⁵ *Phil. Trans.*, 1799.

⁶ *Ann. chim.*, 72, 113 (1809).

⁷ *Pogg. Ann.*, 13, 191 (1828).

⁸ Roscoe and Schorlemmer, Vol. 4, p. 110.

⁹ *Ann.*, 39, 350 (1841).

¹⁰ *Ibid.*, 43, 219 (1842).

¹¹ *Ber.*, 18, 394 (1885).

tained from Them by Hydrolysis.—Following the work of Fourcroy and Vanquelin¹ appeared that of Mulder and his co-workers.² They described the behavior of nitric acid towards a large number of protein substances and gave to the yellow product obtained the name "xanthoproteic-acid." This is the first time that the term "Xanthoproteic" was used in connection with the action of nitric acid on protein material. Vogel³ examined the behavior of nitric acid on silk and later Hrusschauer,⁴ in 1843, continued the investigation with egg-white. Muhlhauser⁵ investigated the behavior of a mixture of nitric and hydrochloric acids on proteins and later, in 1871, Loew⁶ contributed his first paper on the action of sulfuric and nitric acids on protein material. The following year he published further on the same subject⁷ and described characteristic nitrated products. Günsburg⁸ and also Wittich⁹ examined the behavior of albumen towards nitric acid, and Johnson¹⁰ and Osborne have independently shown¹¹ that proteins can enter into ionic reactions with nitric acid. Obermeyer¹² continued the work of Mulder in 1892, being particularly interested in the nature of the aromatic groups of the nitrated protein. He subjected his xanthoprotein to hydrolysis with hydrochloric acid but did not succeed in isolating any characteristic hydrolytic product containing a nitro group. In 1899 appeared the paper of von Fürth,¹³ describing the behavior of nitric acid on casein and horn. Characteristic products were isolated, but Samuely¹⁴ considers that his nitration products and those of Loew¹ are different substances.

Habermann and Ehrenfeld¹⁵ investigated the action of nitric acid on certain proteins and succeeded in isolating hydroxyglutaric acid. Following their work no further attention was paid to the problem of nitra-

¹ *Loc. cit.*

² *Pogg. Ann.*, 37, 594; *Centrbl.*, 1836, 538; *Ann.*, 28, 73; *Centrbl.*, 1838, 885; *Natur u. Scheik Archief*, 1838, 87; *Centrbl.*, 1839, 242; *J. prakt. Chem.*, 20, 340; *Centrbl.*, 1840, 515. Van der Pant, *Scheikung Anderzoek*, 2, 136; *Centrbl.*, 1849, 342.

³ *Buchner's neues Repert.*, 8, 1; *Handwörterbuch der reinen u. angew. Chem.*, 7, 743 (1859).

⁴ *Ann.*, 46, 348 (1843).

⁵ *Ibid.*, 90, 171 (1854); 101, 171.

⁶ *J. prakt. Chem.*, [2] 3, 180.

⁷ *Ibid.*, [2] 5, 433 (1872); *Ber.*, 34, 3560 (1901).

⁸ *Wien. Acad. Ber.*, 45, 643; *Centrbl.*, 1863, 460.

⁹ *J. prakt. Chem.*, 73, 25.

¹⁰ *J. Chem. Soc.*, 27, 734 (1874).

¹¹ *Report Conn. Expt. Station*, 1900, 399; *THIS JOURNAL*, 24, 39 (1902).

¹² *Centrbl. Physiol.*, 6, 300 (1892); *Centrbl.*, 2, 529 (1892); *Jahr.*, 1892, 2113.

¹³ "Einwirkung von Salpetersäure auf Eiweissstoff. Habilitationsschrift," Strassburg, 1899.

¹⁴ *Oppenheimer*, Vol. I, p. 441.

¹⁵ *Z. physiol. Chem.*, 35, 231 (1902).

tion until Kossel and Kennaway,¹ in 1911, investigated the behavior of nitric acid towards the protamine—*Clupein*. This underwent nitration smoothly, giving a nitroclupein, which gave on hydrolysis nitroarginine. Later Inouye² subjected *nitrofibroin* to hydrolysis with sulfuric acid and isolated from the products of hydrolysis what he believed was nitrotyrosine.³ Regarding the structure of this acid, we have no definite knowledge. Recently Mörner⁴ has contributed an interesting paper in which he has described the isolation of a well-characterized sulfur compound obtained by treating sulfur protein with nitric acid. He isolated methyl-sulfuric acid, in the form of its barium salt, $(\text{CH}_3\text{SO}_3)_2\text{Ba} \cdot 1.5\text{H}_2\text{O}$, from the hydrolysis liquors of wool, serum, egg protein, casein, ovomucoid, haemoglobin and gluten. Since cystin does not yield this interesting compound with nitric acid, Mörner's observation, therefore, indicates that there are at least two forms of sulfur linkings in sulfur protein.

The Structure of Nitrotyrosine.

It is evident that before one can hope to formulate definite conclusions regarding the action of nitric acid on proteins, and assign correct structural formulas to the products of hydrolysis containing nitro groups, we must first determine what compounds are formed when the aromatic amino acid constituents of proteins are attacked by this reagent under similar conditions. This involves not only a study of the behavior of nitric acid towards phenylalanine (I), tyrosine (II) and tryptophane (III), but also its action on peptide combinations of these acids and likewise peptides containing these acids in combination with the naturally occurring amino acids of the aliphatic series. The action of nitric acid on tryptophane and peptide combinations containing the above amino acids has never been investigated. Phenylalanine, on the other hand, has been shown by Erlenmeyer and Lipp⁵ to interact smoothly with nitric acid giving the corresponding *p*-nitro derivative represented by Formula IV. So far as the writers are aware, however, this amino acid has never been identified among the hydrolytic products of nitrated proteins. It is not improbable that this is the precursor of *p*-nitrobenzoic acid, which was obtained by Nencki and Sieber⁶ by treatment of different proteins with strong nitric acid. In the case of tyrosine it has been shown by different investigators that this acid and nitric acid interact smoothly under definite conditions forming *mono*-nitrotyrosine. Inouye⁷ likewise obtained what he believed was this same nitro-compound by hydroly-

¹ *Z. physiol. Chem.*, **72**, 486 (1911).

² *Ibid.*, **81**, 80 (1912).

³ Städeler, *Ann.*, **116**, 77 (1860).

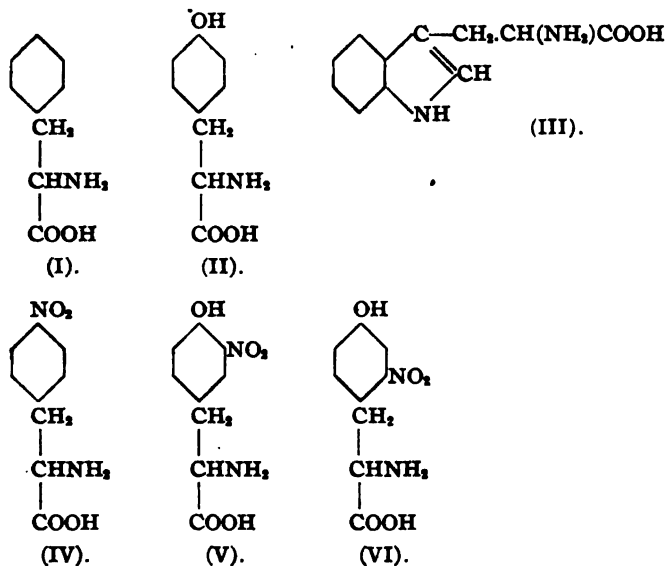
⁴ *Z. physiol. Chem.*, **93**, 175 (1914).

⁵ *Ann.*, **219**, 166 (1883).

⁶ *Ber.*, **18**, 394 (1885).

⁷ *Z. physiol. Chem.*, **81**, 80 (1912).

sis of nitrofibroin with sulfuric acid. He was unable to assign a definite structure to his acid because of the fact that it has never been shown in what position tyrosine (II) is attacked by nitric acid. Two isomeric acids might theoretically be formed in this reaction, namely, 3-nitro- and 2-nitrotyrosine represented by Formulas V and VI, respectively. Whether one or both of these two acids are produced has never been established. The primary object of the work described in this paper was the acquirement of experimental data which would enable us to decide beyond doubt the structure of this interesting nitration product.



That tyrosine will react with nitric acid was apparently first recognized by Warren de la Rue¹ in 1848, who showed that the tyrosine obtained by hydrolysis of cochineal interacts with this reagent giving a new organic acid which, he states, crystallized in the form of needles. No further attention was paid to this observation until 1850, when Strecker² reinvestigated this reaction and showed that tyrosine is completely oxidized by vigorous action of strong nitric acid forming oxalic acid. If dilute acid was used, he found that tyrosine was not oxidized, but underwent nitration smoothly, giving him what he called—"salpetersaures Nitrotyrosin." It is interesting to note here that Strecker did not observe the formation of picric acid in this reaction. Strecker described the hydrochloride and barium and silver salts of nitrotyrosine and even prepared the free amino acid by decomposition of its silver salt with hydrogen sulfide. He states that this crystallized in clusters of radiating

¹ *Ann.*, 64, 35 (1848).

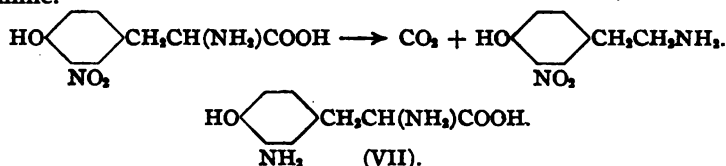
² *Ibid.*, 73, 74 (1850).

needles, which were characterized by the property of giving intensely red solutions when dissolved in aqueous solutions of the alkali metals and ammonia. Strecker did not obtain enough of the amino acid for analysis.

Strecker's observations were confirmed 10 years later by Städeler,¹ who prepared nitrotyrosine according to Strecker's directions. He described the amino acid as a sulfur-yellow substance which had a bitter taste and colored blue litmus red in aqueous solution. He showed that it had both basic and acid properties and described the nitrate, hydrochloride and neutral sulfate of the amino acid. He also tested the stability of the acid on heating and contributed the following statement regarding its behavior under these conditions:

"In stärkerer Hitze tritt schwache Vepuffung ein unter Entwicklung gelbrother Tropfen, die zum Theil zu wenig gefärbten, sternförmig gruppierten Krystallen condensiren."

This change was undoubtedly a normal one in which the acid broke down, on heating, with formation of carbon dioxide and the corresponding amine.



Beyer,² in 1867, prepared nitrotyrosine according to the method of Städeler and subjected it to reduction with tin and hydrochloric acid and obtained the corresponding aminotyrosine. Abderhalden and Masini³ studied the behavior of this amino acid in alcaptonuric patients. Neuberg⁴ considers this acid to have the formula of an ortho derivative represented by Formula VII, but no proof is offered for this. Johnson⁵ has stated in a previous paper that nitrotyrosine is very probably a 3-nitro derivative as represented by Formula V.

The first evidence which was produced to indicate that tyrosine undergoes nitration with formation of more than one nitro derivative was published by Casimir Funk, in 1912, in a paper entitled: "The Constitution of Aminotyrosine and the Action of Oxidases on Some Tyrosine Derivatives."⁶ He claims to have shown that nitrotyrosine, prepared by Strecker and Städeler's method, is not a definite compound, but a mixture of two isomeric amino acids, represented by Formulas V and VI, respec-

¹ *Ann.*, 116, 77 (1860).

² *Z. Chem.*, 10, 436 (1867).

³ *Z. physiol. Chem.*, 66, 140 (1910); 67, 404 (1910).

⁴ Oppenheimer's *Handbuch der Biochemie*, 4, II, 363 (1910).

⁵ Johnson and Bengis, *THIS JOURNAL*, 34, 1054 (1912).

⁶ *J. Chem. Soc.*, 101, 1004 (1912).

tively. Since we have obtained results which do not support Funk's conclusions, it will be necessary, before the discussion of our work, to present briefly here the evidence on which Funk based his conclusions. He reduced his nitrotyrosine to the corresponding aminotyrosine by the action of tin and hydrochloric acid. With the object of converting the latter into 3,4-dihydroxyphenylalanine, he diazotized 10 g. of his diamino acid (melting at 265°) by passing through its aqueous solution the calculated amount of nitrous anhydride and obtained 5 g. of aminotyrosine, having a higher melting point than the original material, namely, 273° . Funk also observed that this differed from the initial acid in stability towards oxidizing agents and concluded, from his observation that it was not changed by the action of specific oxidases (laccase and tyrosinase), that this acid must be considered to be *2-aminotyrosine*, represented by Formula IX. In other words, according to Funk, nitrotyrosine is a mixture of two acids which are transformed on reduction into a mixture of two corresponding aminotyrosines. By the action of nitrous acid on this mixture 3-aminotyrosine (VII) is destroyed, while 2-aminotyrosine (IX) is left unchanged in the solution. Funk apparently did not consider the fact that an aminotyrosine contains two amino groups which are susceptible to attack by nitrous acid and that part of his original amino acid may have been converted into an α -hydroxy acid represented by Formula X or XI. Such a change would be perfectly analogous to that observed by Erlenmeyer and Lipp,¹ who showed that *p*-aminophenylalanine is converted into a mixture of tyrosine and the isomeric α -hydroxy acid, $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{OH})\text{COOH}$, by the action of nitrous acid.

Furthermore, Funk states, in the experimental part of his paper, that 0.5 g. of his pure 2-aminotyrosine (IX) gave 0.9 g. of the corresponding tribenzoyl derivative by application of Schotten and Baumann's reaction, which is a yield of 80% of the theoretical. On the other hand, when the same reaction was applied with crude aminotyrosine, he obtained only a very small amount of the same tribenzoyl compound. From these results the following conclusion can therefore be drawn: Ten grams of crude aminotyrosine yield 50% of its weight in 2-aminotyrosine, which is not acted upon by nitrous acid, and from which can be obtained a yield of the tribenzoyl compound corresponding to 80% of the theoretical. The initial aminotyrosine, however, gives only a small amount of the same acyl derivative. These results are somewhat contradictory. Later Funk and Macallum,² in a paper entitled: "The Chemical Nature of Substances from Alcoholic Extracts of Various Foodstuffs which Give a Color Reaction with Phosphotungstic and Phosphomolybdic Acids,"

¹ *Loc. cit.*

² *Biochem. J.*, 7, 356 (1913).

stated that both 2-amino- and 3-aminotyrosine react with Folin's¹ uric acid reagent (phosphotungstic acid) and with Folin's polyphenol reagent (phosphomolybdic acid) giving positive tests. Yet they did not mention the source of either compound. They found that nitrotyrosine failed to react with either reagent.

We have now obtained new experimental evidence which proves conclusively that, when tyrosine is subjected to nitration according to the conditions recommended by Strecker and Städeler,² it is converted into a mixture of two isomeric nitro acids represented by Formulas V and VI. The chief product of the reaction is not 2-nitrotyrosine (VI) as concluded by Funk, but the isomeric modification (V). In fact, the proportion of the isomer (VI) was so small that it was possible by one reaction only to show that it actually is a product of nitration.

When crude nitrotyrosine is methylated by digestion with methyl iodide in methyl alcohol solution and in the presence of an excess of potassium hydroxide, the hydroxy group remains unchanged and the amino acid is converted into a mixture of two substances—the normal quaternary salt represented by Formula XII, and a secondary product which we have expressed by Formula XIII. The normal salt (XII), however, is the chief product of the reaction. Körner and Menozzi³ applied the same reaction to tyrosine and obtained the salt (XVI). In the nitrotyrosine, therefore, the nitro group affords a protection for the hydroxyl radicle in such reactions. Apparently we are dealing here with a tautomeric change which involves a rearrangement of the true nitrophenol into its pseudo modification (XVIII) in the presence of alkali, forming the colored salt represented by Formula XIX. Such an assumption is in strict accord with the work of Hantzsch,⁴ Hewitt, Johnson and Pope⁵ and Meldola and Holley⁶ on the structure of the salts of *o*-nitrophenols. That the oxygen ethers of *o*-nitrophenol combinations are easily hydrolyzed in the presence of alkalis, was observed by Miller and Kinkelin,⁷ who showed, for example, that the methyl ester of *o*-methoxy-*m*-nitrocinnamic acid is completely saponified by warming with sodium hydroxide and even sodium carbonate in dilute alcohol solution, forming the corresponding *o*-hydroxy-*m*-nitrocinnamic acid.

The quaternary iodide (XII) and the di-quaternary compound (XIII) are both decomposed by vigorous boiling with strong sodium hydroxide solution with evolution of trimethylamine and formation of 3-nitro-4-

¹ *J. Biol. Chem.*, 11, 265 (1912).

² *Loc. cit.*

³ *Gazz. chim. ital.*, 11, 550 (1881).

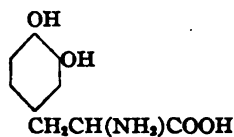
⁴ *Ber.*, 39, 1073 (1906); 40, 330 (1907).

⁵ *J. Chem. Soc.*, 103, 1626 (1913).

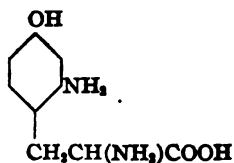
⁶ *Ibid.*, 105, 410 (1914).

⁷ *Ber.*, 22, 1705 (1889).

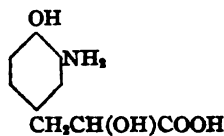
hydroxycinnamic acid (XIV), melting at 223° . A description of the cinnamic acid has recently been given in a paper by Johnson and Kohmann.¹



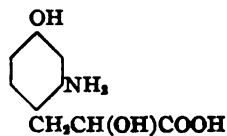
(VIII).



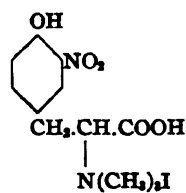
(IX).



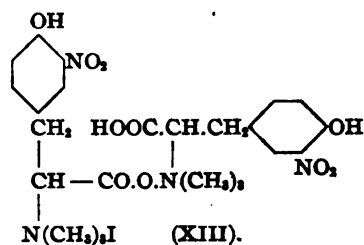
(X).



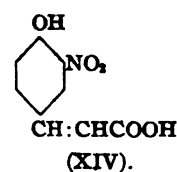
(XI).



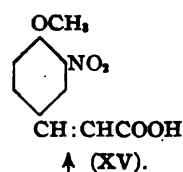
(XII).



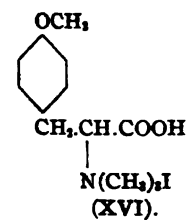
(XIII).



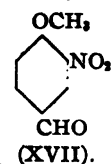
(XIV).



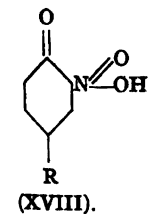
(XV).



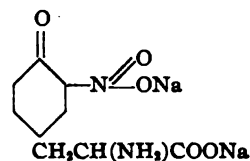
(XVI).



(XVII).



(XVIII).



(XIX).

¹ THIS JOURNAL, 37, 162 (1915).

We obtained no evidence of the formation of the isomeric 2-nitro-4-hydroxycinnamic acid.

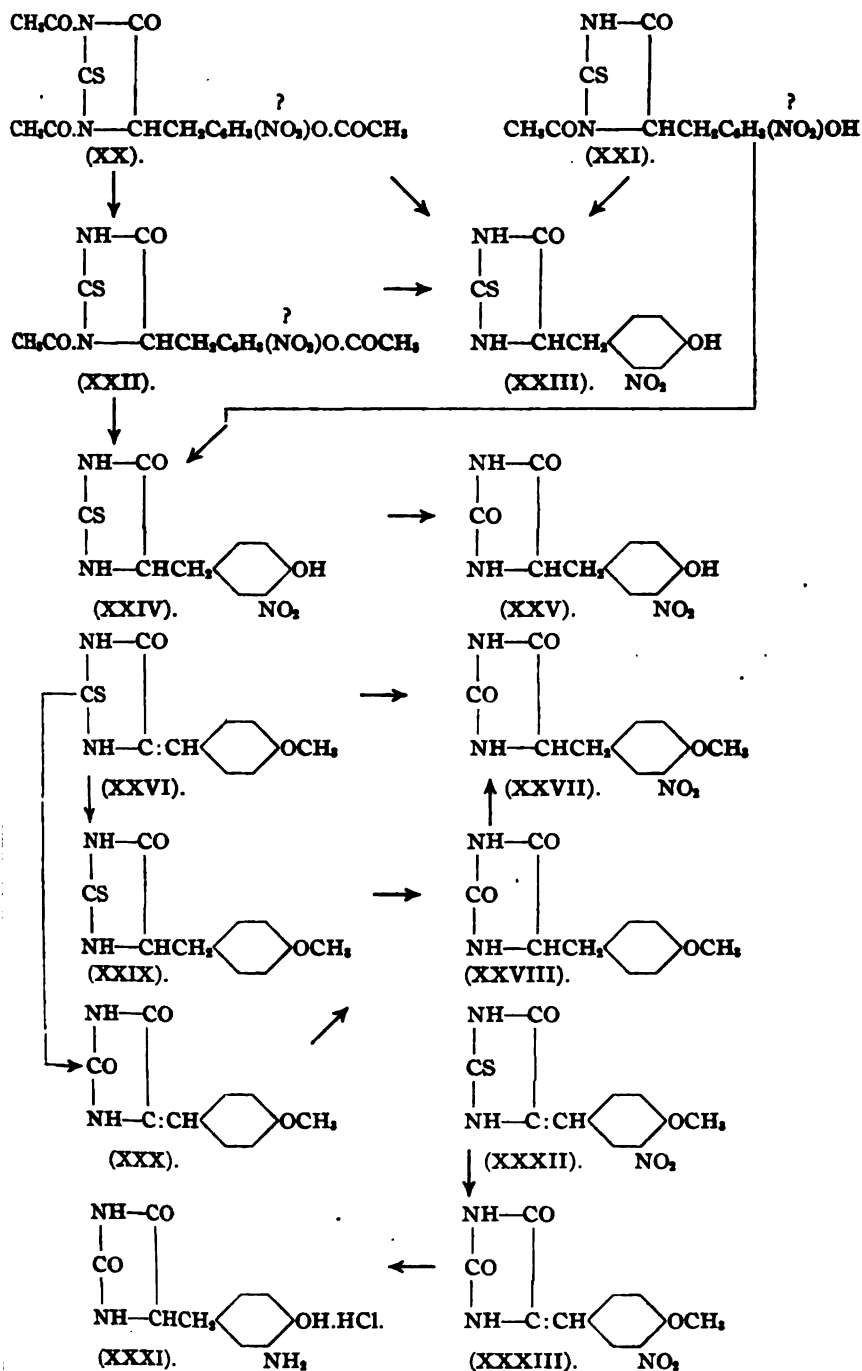
Nitrotyrosine, prepared from tyrosine, interacts smoothly with ammonium thiocyanate in acetic anhydride solution, forming different products, depending apparently on the length of time of heating.

We succeeded in isolating three types of combinations, namely, mono-, di- and triacetyl derivatives, which were all impure and mixtures of isomeric hydantoins. The triacetyl derivative (XX) was easily hydrolyzed by boiling with acetic acid, forming the corresponding diacetyl compound (XXII). That our diacetyl hydantoin (XXII) and monoacetyl compounds (XXI) were mixtures, was established by the fact that both compounds underwent hydrolysis, when digested with hydrochloric acid, giving the two isomeric thiohydantoins, namely, 2-thio-4-(2-nitro-4-hydroxybenzyl)-hydantoin and 2-thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin, represented by Formulas XXIII and XXIV, respectively. Since the hydantoin (XXIV) was obtained in excellent yields in every case and was accompanied by only a small amount of the isomeric thiohydantoin, we conclude that the original nitrotyrosine, from which they were derived, is chiefly a 3-nitro derivative as represented by Formula V. *Tyrosine therefore undergoes nitration with formation of two isomeric nitrotyrosines. That modification, in which the nitro group is substituted in the nucleus, ortho to the hydroxyl group, is the chief product of the reaction.*

The structure of the thiohydantoin (XXIV) was established in the following manner: 2-Thiohydantoin was first condensed with anisic aldehyde with formation of 2-thio-4-anisaldehydantoin (XXVI). This was then converted into 4-anisylhydantoin (XXVIII) by two methods. It was either reduced to the thioanisylhydantoin (XXIX) and then desulfurized by digestion with chloroacetic acid, or first desulfurized with formation of (XXX) and the latter finally reduced to the saturated hydantoin (XXVIII). Johnson and Bengis¹ have already shown that this hydantoin (XXVIII) reacts with nitric acid with formation of 4-(3-nitro-4-methoxybenzyl) hydantoin (XXVII). We now find that this hydantoin (XXVII) is easily demethylated by heating with hydrobromic acid in glacial acetic acid solution, giving the same hydantoin (XXV), as is formed by desulfurization of 2-thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin (XXIV) with chloroacetic acid.

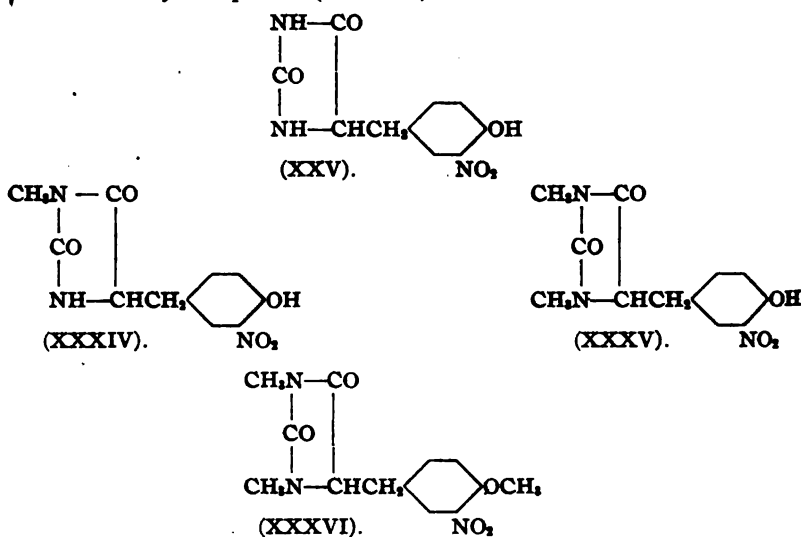
The structure of the hydantoin was also established as follows: The 2-thiohydantoin (XXIV), which was prepared by the action of ammonium thiocyanate on nitrotyrosine, was first desulfurized in the usual manner and the resulting hydantoin (XXV) then reduced to the corresponding aminohydantoin (XXXI). This was isolated in the form of its hydrochloric acid salt. The latter proved to be identical with the hydrochloric acid

¹ THIS JOURNAL, 34, 1056 (1912).



salt of the hydantoin of aminotyrosine, which was synthesized in the following manner: 2-Thio-3-benzoylhydantoin, which is easily obtained according to the method of Johnson and Nicolet,¹ was condensed with 3-nitroanisic aldehyde (XVII)² when 2-thio-4-nitroanisalhydantoin (XXXII) was formed. This was then desulfurized and the resulting hydantoin (XXXIII) reduced with hydriodic acid, and red phosphorus when the hydriodic acid salt of the aminohydantoin was obtained. On digesting this salt with silver chloride it was converted into the corresponding hydrochloride represented by Formula XXXI. The hydantoin and 2-thiohydantoin of 2-nitrotyrosine have not been synthesized.

Especially interesting was the behavior of the hydantoin of 3-nitrotyrosine (XXV) on alkylation. It behaved in a similar manner as the free amino acid in that the hydroxyl group was protected against alkylation by the presence of the *ortho* nitro group. When treated with one molecular proportion of methyl iodide the *mono*-allyl derivative (XXXIV) was formed. When an excess of methyl iodide was used the dialkyl derivative (XXXV) was formed. We obtained no evidence of the formation of the methoxy compound (XXXVI).



Experimental.

Preparation of Tyrosine.—The tyrosine which was used in this investigation was obtained by the hydrolysis of silk noils according to the directions given by Fischer.³ Noils is a commercial name assigned to a waste product in the silk industry resulting from the combing of silk

¹ THIS JOURNAL, 33, 1973 (1911).

² Einhorn and Grabfield, *Ann.*, 243, 370 (1888).

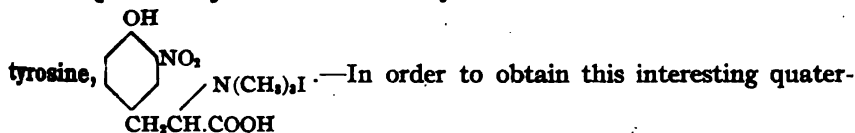
³ *Z. physiol. Chem.*, 33, 181 (1901).

and consists of short fibers of nearly pure *fibroin*.¹ The noils yielded on hydrolysis about 7-8% of their weight in tyrosine. The tyrosine was purified by digesting with glacial acetic acid to remove any leucine present and then recrystallized from boiling water.

Preparation of Nitrotyrosine.—The nitrotyrosine was prepared according to the method described by Städeler.² The following procedure was generally followed: Sixteen grams of tyrosine were first suspended in 85 cc. of water and 43 g. of nitric acid (sp. gr. 1.42) were then added slowly while the acid mixture was kept cold by means of an ice bath. The tyrosine completely dissolved and after allowing to stand in an ice bath for 12 hours 19 g. of the nitrate of nitrotyrosine finally separated. After filtering by suction the salt was either first allowed to dry in the air or suspended immediately in 60 cc. of cold water and ammonia added slowly to liberate nitrotyrosine, which generally first separated in an amorphous form. This soon assumed a crystalline condition, however, and was filtered off and washed with cold water. The yield of crude material was about 13 g. This amino acid was used for the following experiments without any further purification.

Inouye³ states that his nitrotyrosine, which he obtained by hydrolysis of nitrofibroin, gave a red color when warmed with Millon's reagent. It has been our experience that this test is not successful in this case unless special precautions are taken in its application. The color at best is not as strong as that obtained in the case of tyrosine and if too much heat is applied the color is completely destroyed or will not develop. The same considerations hold on applying the test with the hydantoin derivatives of nitrotyrosine. The first effect in general was the production of a yellow color which gradually assumed a red color by gentle warming. This was stronger in some cases than others. If very small amounts were taken the color did not develop. Furthermore, the red color was generally more pronounced when viewed by reflected light.

The Quaternary Salt: Trimethylammonium Iodide of *o*-Nitro-



nary salt the following procedure was adopted: Five and seven-tenths grams of the crude nitrotyrosine were dissolved in 150 cc. of methyl alcohol, containing in solution 7 g. of pure potassium hydroxide. A

¹ Note.—For our supply of silk we are indebted to the Cheney Brothers, silk manufacturers of South Manchester, Connecticut. We take this opportunity to express our appreciation of their interest in our work and willingness to cooperate with us.—T. B. J.

² *Loc. cit.*

deep red solution was obtained. Thirty-four grams of methyl iodide were then added and the mixture digested gently, under a reflux condenser, for about 18–19 hours. The reaction was then apparently complete. The excess of alcohol and methyl iodide was evaporated by heating on a water bath and the residue obtained dissolved in about 50 cc. of hot water and the solution decolorized by digestion with bone-coal. On cooling, the quaternary salt began to separate immediately in the form of radiating crystals. After standing for a long time, however, it was observed that a second product likewise crystallized out in the form of short, stout prisms. In order to isolate these two characteristic products an application was made of a fractional crystallization, when there were obtained by cooling to room temperature about 4.9 g. of yellow crystalline material. This was identified as the quaternary derivative of *o*-nitrotyrosine and was purified by crystallization from alcohol, from which it separated, on cooling, in radiating clusters of yellow prisms. After three recrystallizations from alcohol we obtained 3 g. of the salt having a constant melting point of 119° and decomposing at 121° . The salt was dried for analysis by heating at 100° . It contained two molecules of water of crystallization. This could not be determined, however, because the salt slowly underwent decomposition when heated at a temperature sufficiently high to remove the water. It gave Millon's test.

Calc. for $C_{12}H_{17}O_5N_2I \cdot 2H_2O$: N, 6.48; I, 29.38.

Found: N, 6.51, 6.48, 6.57, 6.47, 6.43; I, 29.00, 29.43, 29.7, 29.5.

The Diquaternary Salt (XIII).—As stated above, after the separation of the quaternary salt just described, a second crop of crystals was obtained on standing. These were more granular and had a pronounced prismatic habit. It is very slow in separating and generally deposits on the sides and bottom of the beaker. In one experiment four successive crops were filtered off and all found to be identical. This compound, whose structure we have provisionally represented by Formula XIII, crystallizes from hot 95% alcohol in clusters of stout prisms which melt at 220 – 221° with decomposition. For analysis it was dried at 110° . The salt responded to Millon's test.

Calc. for $C_{24}H_{35}O_{10}N_4I$: N, 8.43; I, 19.1.

Found: N, 8.49, 8.48, 8.43; I, 18.82, 18.87.

In another experiment we obtained from 3.7 g. of recrystallized nitrotyrosine, 3.8 g. of the quaternary salt melting at 119° and 0.9 g. of the diquaternary compound melting at 220 – 221° . These observations were very uniformly duplicated when nitrotyrosine was exhaustively alkylated with methyl iodide.

Proof of the Structure of *o*-Nitrotyrosine. The Formation of 3-Nitro-4-hydroxycinnamic Acid (XIV) by the Action of Alkali on the Quater-

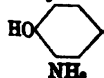
nary Salt (XII).—Two grams of the quaternary salt (XII) were dissolved in 50 cc. of 10% sodium hydroxide solution. The bright red solution was then boiled by immersing the flask in an oil bath. The salt was decomposed by this treatment with evolution of trimethylamine and a bright red sodium salt separated from the hot solution. This was filtered off and examined. It was very soluble in water and insoluble in alcohol. When alcohol was added to its aqueous solution the salt was precipitated in an amorphous condition. In order to obtain the free acid the salt was dissolved in water and the solution acidified with hydrochloric acid, when the above cinnamic acid separated. The yield was 0.75 g. or 78% of a theoretical yield. The acid was insoluble in cold water but slightly soluble in hot, from which it crystallized in long, colorless needles. It was soluble in hot alcohol and crystallized from this solvent in yellow needles arranged in bundles. The acid responded to Millon's test and melted at 223° with decomposition. It was identical with 3-nitro-4-hydroxycinnamic acid, which has recently been described in a paper by Johnson and Kohmann.¹ A mixture of the two acids melted at 223° . It was dried for analysis at 110° .

Calc. for $C_9H_7O_3N$: N, 6.70. Found: N, 6.72, 6.57.

The mother liquor from the red salt was heated in the oil bath for a long time, or until practically no more trimethylamine was evolved. The solution was then cooled and acidified, when a small amount of the cinnamic acid separated. This was separated and the filtrate concentrated and examined further, but we obtained no evidence of the presence of any other acid.

The Formation of 3-Nitro-4-hydroxycinnamic Acid (XIV) by the Action of Alkali on the Diquaternary Derivative (XIII).—By application of the above treatment with 10% sodium hydroxide to the diquaternary salt XIII, 3-nitro-4-hydroxycinnamic acid was also obtained. It melted at 223° . The smoothness of these transformations is well brought out by the following results obtained in one experiment: Sixteen grams of crude nitrotyrosine yielded 10 g. of the quaternary salt and 6 g. of the diquaternary compound. The former yielded on hydrolysis with sodium hydroxide 4.5 g. of the cinnamic acid or 92% of the theoretical yield, while the diquaternary salt gave 3 g. of the unsaturated acid or 79% of the theoretical yield. All the filtrates were again carefully examined, but here again we obtained no evidence of the presence of an isomeric acid.

Hydrochloride of 3-Amino-4-hydroxycinnamic Acid,

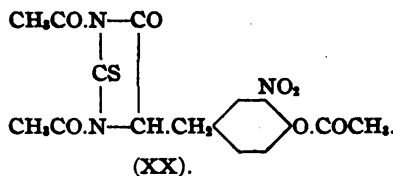
 $\text{CH} = \text{CH} \cdot \text{COOH} \cdot \text{HCl}$.—This salt was obtained by digesting

¹ *Loc. cit.*

the above nitrohydroxycinnamic acid on a steam bath with tin and dilute hydrochloric acid. The nitro-compound underwent reduction smoothly and completely dissolved. After filtering from the excess of tin and cooling, the hydrochloride of the amino acid then separated in the form of colorless needles. The salt was purified by recrystallization from dilute hydrochloric acid. When heated in a capillary tube it began to undergo a change at 225° and at 240° decomposed with effervescence.

Calculated for $C_9H_9O_3N.HCl$: N, 6.51. Found: N, 6.55.

The Action of Nitrotyrosine on Ammonium Thiocyanate in Acetic Anhydride Solution.—Nitrotyrosine exhibits a strong tendency to interact with ammonium thiocyanate and acetic anhydride and various products can be obtained depending upon the conditions employed. In one experiment, twelve grams of crude nitrotyrosine (from tyrosine), 6.3 g. of anhydrous ammonium thiocyanate and 60 cc. of acetic anhydride were mixed in a flask and then heated on a steam bath. On warming gently at first there was an immediate reaction and a clear, orange-colored solution was obtained. Heating was continued for 20 minutes, when the mixture was cooled and finally poured into 400 cc. of cold water. (See below for an examination of this water solution.) A red oil separated which finally solidified. The yield was 14.5 g. This substance was found to be soluble in hot alcohol and in ether, and recrystallized from the former solvent in needles or slender prisms. This solvent, however, was not used for purification. This was accomplished by dissolving the 14.5 g. in 100 cc. of glacial acetic acid and then digesting with a little bone-coal to clarify the solution. On cooling, only 0.2 g. of yellow needles deposited. This product appeared to be a perfectly definite compound and after washing with pure acetic acid was dried for analysis. It melted at 174° . A nitrogen determination agreed with the calculated value for a triacetyl derivative of the thiohydantoin of nitrotyrosine (XX). This is the first



case where we have observed the formation of a thiohydantoin containing acetyl groups attached to both nitrogen atoms of the ring, by application of the ammonium thiocyanate reaction. The result obtained by analysis indicated that the hydantoin crystallized with a molecule of acetic acid.

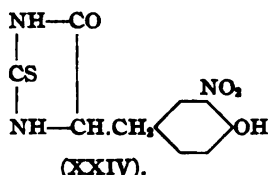
Calc. for $C_{14}H_{14}O_7N_2S.CH_3COOH$: N, 9.27. Found: N, 9.25.

2-Thio-3-acetyl-4-(3-nitro-4-acetoxybenzyl)-hydantoin (XXII).—The acetic acid filtrate left after filtering off the above triacetyl compound was

concentrated to a volume of 20 cc. and cooled when 2.7 g. of this diacetyl compound separated in the form of a fine powder. It was purified by re-crystallization from glacial acetic acid and deposited as yellow, rectangular plates which melted at 173–175°. The hydantoin was dried for analysis by heating to constant weight at 110°.

Calc. for $C_{14}H_{15}O_4N_2S$: N, 11.97. Found: N, 11.75.

Having established the presence of these two acetyl derivatives, all the acetic acid filtrates were finally combined and evaporated to dryness on a steam bath. The crystalline residue which was left behind was then digested for one and one-half hours with an excess of concentrated hydrochloric acid and the solution finally evaporated to dryness. The acetyl groups were all removed by this treatment and we obtained the crude thiohydantoin in the form of a yellow powder mixed with a gummy substance which adhered to the sides of the evaporating dish (see below). The yellow powder was identified as 2-thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin (XXIV).



It was purified by crystallization from glacial acetic acid and separated, on cooling, in the form of hexagonal plates which melted at 239–242° with decomposition. The compound has a yellow color and is practically insoluble in water and difficultly soluble in alcohol.

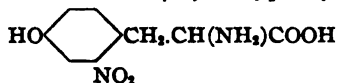
Calc. for $C_{16}H_{17}O_5N_3S$: N, 15.74. Found: N, 15.60.

2-Thio-4-(2-nitro-4-hydroxybenzyl)-hydantoin (XXIII). — The red, gummy material described in the previous experiment was separated mechanically and dissolved in glacial acetic acid. On cooling this solution rapidly, the hydantoin separated in the form of yellow needles. The yield was very small, being only about 0.1 g. This material was identified as the isomeric hydantoin represented by Formula XXIII, and was formed by action of ammonium thiocyanate on 2-nitrotyrosine which is formed in small amount by the action of nitric acid on tyrosine. The yellow color of the hydantoin is due to the fact that it crystallizes with one molecule of acetic acid. In fact, it readily loses this acid when heated at 110°, giving the plain hydantoin, which is a brick-red compound. The hydantoin has no definite melting point, but begins to char when heated to 270° and gradually undergoes further decomposition when heated above this temperature. An acetic acid determination was made with the following result:

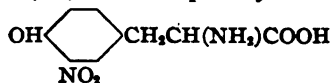
0.0691 g. substance lost at 110° 0.0111 g. CH_3COOH .

Calc. for $C_{16}H_{17}O_5N_3S \cdot \text{CH}_3\text{COOH}$: CH_3COOH , 16.3. Found: 16.1.

The identification of this characteristic thiohydantoin was the first evidence that tyrosine interacts with nitric acid with formation of a small amount of *2-nitro-4-hydroxyphenylalanine* (VI). Consequently it was very



(VI).



(V).

important to search carefully all filtrates in order to determine whether more of this compound could be obtained for a more thorough examination. We therefore turned our attention to the aqueous solution obtained after pouring the original condensation solution (acetic anhydride + NH_4SCN + crude nitrotyrosine) into cold water. It was first evaporated to dryness and the residue, consisting of a mixture of ammonium thiocyanate, ammonium acetate and thiohydantoin, was then dissolved in an excess of hydrochloric acid. The latter solution was again evaporated to dryness in order to hydrolyze completely any acylhydantoin and the resulting product dissolved in a small volume of glacial acetic acid. To our surprise, on allowing the solution to cool, we obtained a fine crop of yellow needles arranged in rosettes mixed with a small amount of red blocks or stout prisms. The two forms were easily separated mechanically. The yellow material was identified as the *2-thiohydantoin* of *2-nitro-4-hydroxyphenylalanine* containing a molecule of acetic acid of crystallization. When heated at 110° it lost its yellow color, became brighter red and melted when heated above 274° with decomposition.

Calc. for $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_3\text{S}$: N, 15.74. Found: N, 15.9.

The red blocks decomposed at the same temperature as the yellow modification containing acetic acid of crystallization.

In order to be absolutely certain that tyrosine is converted by nitration into a mixture of two isomeric nitro derivatives—*2-nitro-* and *3-nitro-*tyrosines—the ammonium thiocyanate reaction was again applied with crude nitrotyrosine. In this experiment 12.7 g. of the nitrotyrosine, 6.5 g. of ammonium thiocyanate and 64 cc. of acetic anhydride were used and the mixture heated as in previous experiments for 20 minutes. After cooling, the reaction mixture was then poured into water when an oil separated which soon solidified. The weight of this material in this case was 16 g. It was very soluble in warm ether, alcohol and glacial acetic acid. Instead of first crystallizing this crude product from glacial acetic acid, as was done in the previous experiment, this time we dissolved it in hot 95% alcohol. On cooling we obtained neither a *triacetyl* nor a *diacetyl* compound as before, but a product deposited in the form of clusters of flat prisms, which melted at $176\text{--}178^\circ$. The substance apparently underwent a change at this temperature, because if the temperature was held at $176\text{--}177^\circ$ the compound gradually assumed a solid form again

and then melted at 187–188° to a red oil. This compound contained sulfur, was bright yellow in color, and was identified as chiefly *2-thio-3-acetyl-4-(3-nitro-4-hydroxybenzyl)-hydantoin* (XXI). Mixtures of this hydantoin with the triacetyl and diacetyl derivatives represented by Formulas XX and XXII, respectively, melted below 160°. The hydantoin was dried for analysis by heating at 112°.

Calc. for $C_{12}H_{11}O_4N_2S$: N, 13.58. Found: N, 13.25.

When this acetylhydantoin was suspended in strong hydrochloric acid and the mixture heated, it underwent hydrolysis and was converted smoothly into *2-thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin* (XXIV). This was purified by crystallization from hot glacial acetic acid and separated, on cooling, in the form of yellow prisms which decomposed from 239–242°, according to the rate of heating.

After separation of the above acetylhydantoin the alcoholic filtrates were combined and concentrated to a small volume and cooled. At first a few needles deposited which were separated mechanically and discarded. Then we obtained a deposit of rosettes of yellow needles and finally a crop of red prisms. These two latter products were identified as *2-thio-4-(2-nitro-4-hydroxybenzyl)-hydantoin* containing acetic acid of crystallization and the free thiohydantoin (XXIII), respectively. The combined yield was 0.5 g. and both forms decomposed at about 270° without further purification. Both forms dissolved in hot glacial acetic acid and also could be recovered by cooling. Rapid cooling favored the formation of the yellow modification and slow cooling the red form. In fact, both forms deposited together by proper regulation of the conditions. When the yellow modification was heated at 112° acetic acid was driven off and the red hydantoin was obtained. Both modifications melted after purification at 273–274° with decomposition.

0.1047 g. hydantoin lost at 112° 0.0195 g. CH_3COOH .

Calc. for $C_{10}H_9O_4N_2S \cdot CH_3COOH$: CH_3COOH , 18.35. Found: 18.6.

Nitrogen determination in pure hydantoin:

Calc. for $C_{10}H_9O_4N_2S$: N, 15.74. Found: N, 15.60, 15.75.

4-(3-Nitro-4-hydroxybenzyl)-hydantoin (XXV).—In order to obtain this hydantoin, 8.7 g. of the corresponding 2-thiohydantoin were suspended in a solution of 30 g. of chloroacetic acid dissolved in 90 cc. of water and the mixture digested for 6.5 hours. After one hour's treatment the thiohydantoin had completely dissolved. After completion of the reaction the acid solution was then cooled, when this new hydantoin separated in the form of rosettes of yellow needles. The yield was 7.7 g. The hydantoin was purified by crystallization from glacial acetic acid, from which it separated as yellow needles melting at 225–226° to a clear oil. This experiment was repeated and a quantitative yield of the hydantoin was obtained.

The hydantoin crystallized with a molecule of acetic acid. This was lost by heating at 110° . The hydantoin gave Millon's test.

0.8850 g. lost at 110° 0.1731 g. of CH_3COOH .

Calc. for $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2 \cdot \text{CH}_3\text{COOH}$: CH_3COOH , 19.3. Found: 19.5.

Calc. for $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2$: N, 16.75. Found: N, 16.66.

This same hydantoin was obtained by demethylation of 4-(3-nitro-4-methoxybenzyl)-hydantoin (XXVII).¹ For example, 3 g. of this hydantoin were heated in a bomb tube at 100° for 3 hours with 50 cc. of glacial acetic acid, which had been saturated at 0° with hydrobromic acid gas. On opening the tube a clear solution was obtained. On allowing this to stand, about 0.5 g. of a difficultly soluble product separated which did not melt at 300° . This was separated and the acid solution evaporated to dryness under diminished pressure. The residue was then dissolved in hot water, separated by crystallization, and finally recrystallized again from acetic acid. It deposited from this solvent in the form of rosettes of needles which melted at $223-4^{\circ}$. A mixture of this with some of the above hydantoin of *o*-nitrotyrosine melted at $223-4^{\circ}$. Therefore, the two compounds were identical. This same experiment was repeated with 3 g. of the methoxyhydantoin and the same result again obtained. The hydantoin crystallized in rosettes of needles and melted at $223-225^{\circ}$. It was identical in every respect with the hydantoin prepared from nitrotyrosine.

Calc. for $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2$: N, 16.75. Found: N, 16.55.

2-Thio-4-(3-nitro-4-methoxybenzal)-hydantoin (XXXII).—In order to obtain this compound 10 g. of 2-thio-3-benzoylhydantoin² and 8.2 g. of nitroanisic aldehyde were heated with 16 g. of anhydrous sodium acetate and 50 cc. of glacial acetic acid for 2.5 hours at 155° . On cooling, the fluid completely solidified. This was then thoroughly disintegrated by treatment with 500 cc. of water and the insoluble hydantoin separated by filtration. The yield was 10 g. The hydantoin was very soluble in alcohol and precipitated in a gelatinous condition by dilution with water. If this gelatinous precipitate was redissolved in dilute alcohol and the solution cooled slowly the hydantoin then separated in star-shaped crystals. It crystallized from dilute acetic acid as flat prisms. When heated in a capillary tube the compound began to darken at 240° and then decomposed at 255° with effervescence.

Calc. for $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_2\text{S}$: N, 15.05. Found: N, 14.95, 14.92.

4-(3-Nitro-4-methoxybenzal)-hydantoin (XXXIII).—This compound has previously been described by Johnson and Bengis.³ We obtained the same hydantoin by digesting the above 2-thiohydantoin (XXXII) with a

¹ Johnson and Bengis, *Loc. cit.*

² Johnson and Nicolet, *Loc. cit.*

³ *Loc. cit.*

28% solution of choroacetic acid. It crystallized from glacial acetic acid in slender, yellow prisms which partially decomposed at 278° and then effervesced at 284° . From 6 g. of the thio compound we obtained 4.6 g. of the hydantoin. Acetic acid determination:

Calc. for $C_{11}H_9O_4N_2 \cdot CH_3COOH$: CH_3COOH , 18.57. Found: 18.48.

Calc. for $C_{11}H_9O_4N_2$: N, 15.97. Found: N, 15.95.

Hydrochloride of 4-(3-Amino-4-hydroxybenzyl)-hydantoin (XXXI).—This salt was obtained by digesting 3 g. of the above benzalhydantoin (XXXIII) with 15 cc. of hydriodic acid and 1.5 g. of red phosphorus. After evaporation of the excess of hydriodic acid the salt was dissolved in water and digested with an excess of silver chloride to precipitate silver iodide and form the hydrochloride. After filtering from silver halides and evaporation of the solution the hydrochloride was crystallized from 20% hydrochloric acid. It separated on cooling as burrs of small prisms which decomposed at about 285° . It crystallized from hydrochloric acid in an anhydrous condition while Johnson and Bengis¹ observed it to crystallize from water with one molecule of water. The same salt was also obtained when the hydantoin of nitrotyrosine (prepared by nitration of tyrosine) was reduced with hydriodic acid and red phosphorus and the resulting hydriodide digested with silver chloride. The hydrochlorides crystallized in the same manner and a mixture of the two behaved as a definite substance when heated in a capillary tube. The melting point was not lowered.

1-Methyl-4-(3-nitro-4-hydroxybenzyl)-hydantoin (XXXIV).—One gram of the hydantoin of *o*-nitrotyrosine (XXV) and one molecular proportion of methyl iodide were dissolved in 30 cc. of methyl alcohol containing 0.22 g. of potassium hydroxide and the mixture heated on the steam bath, with reflux condenser, for 4 hours. On cooling the solution, 0.8 g. of the potassium salt of the unaltered hydantoin separated, showing that practically no reaction took place under these conditions. The experiment was repeated with the same proportions, but heated at 150 – 155° for two hours in a pressure tube. The alcohol solution was then concentrated and finally diluted with water, when the above hydantoin separated as an oil. This dissolved in hot water and separated, on cooling, as an oil which soon solidified. It crystallized in yellow balls of minute prisms, which melted at 202° to a clear oil. It gave a red color with Millon's reagent.

Calc. for $C_{11}H_{11}O_4N_2$: N, 15.85. Found: N, 15.9.

1,3-Dimethyl-4-(3-nitro-4-hydroxybenzyl)-hydantoin (XXXV).—This was prepared by heating the hydantoin of *o*-tyrosine (XXV) in methyl alcohol solution with 3 molecular proportions of potassium hydroxide and 4 of methyl iodide for 2 hours at 155° . On pouring the alcohol solution

¹ *Loc. cit.*

into cold water the hydantoin separated. It was purified by recrystallization from dilute alcohol and separated in the form of balls of microscopic crystals. The compound melted from 180–185° and gave a positive test with Millon's reagent. It was dried for analysis at 110°.

Calc. for $C_{12}H_{12}O_2N_2$: N, 15.06. Found: N, 15.22, 15.20.

2-Thio-4-anisalhydantoin (XXVI).—Johnson and O'Brien¹ first prepared this compound by condensing 2-thio-3-benzoylhydantoin with anisic aldehyde and finally hydrolyzing the resulting benzoyl derivative with hydrochloric acid. The same compound was prepared for our work by condensing 2-thiohydantoin with anisic aldehyde in acetic acid solution and in the presence of sodium acetate. From 23 g. of the 2-thiohydantoin we obtained 45 g. of the anisal compound. It was crystallized from glacial acetic acid and melted at 260°.

Calc. for $C_{11}H_{10}O_2N_2S$: N, 11.96. Found: N, 11.95.

2-Thio-4-anisylhydantoin (XXIX).—The hydantoin was prepared by reduction of the above anisalhydantoin (XXVI) with sodium amalgam. The procedure was as follows: Five grams of the unsaturated hydantoin were suspended in a solution of 65 cc. of water and 10 cc. of dilute sodium hydroxide and then 100 g. of 3% sodium amalgam added in small portions at a time. The temperature was kept at 75°. After the amalgam had been added the solution was then filtered and acidified with hydrochloric acid, when the hydantoin separated in a crystalline condition. The yield of crude material was 4.5 g. In order to destroy any hydantoic acid present this material was suspended in hydrochloric acid and the mixture heated on the steam bath. The acid was finally completely evaporated and the hydantoin purified by crystallization from acetic acid. It separated from this solvent in plates and melted at 215°.

Calc. for $C_{11}H_{12}O_2N_2S$: N, 11.87. Found: N, 12.0, 11.92.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE USE OF CYANIC ACID IN GLACIAL ACETIC ACID SOLUTION, AND IN MIXTURES OF GLACIAL ACETIC ACID WITH OTHER ORGANIC SOLVENTS. DERIVATIVES OF 1-ISOBUTYRIC ACID AMINO-5-DIMETHYLHYDANTOIN.

BY J. R. BAILEY AND W. T. READ.

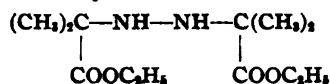
Received June 12, 1915.

Introduction.

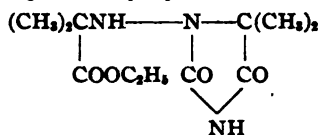
As is well known, many reactions in organic chemistry have been found to proceed most smoothly in glacial acetic acid, and this cannot, in every

¹ *Loc. cit.*

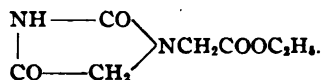
instance, be ascribed to the mere fact that the glacial acetic acid is a better solvent than other media for the reacting constituents. Water-free acetic acid is beyond doubt in many cases a direct catalyst. In the work herein described, the observation has been made that cyanic acid does not react with ethyl hydrazoisobutyrate



in water solution, but in glacial acetic acid, the two substances at room temperature condense readily with the formation of the ethyl ester of 1-isobutyric acid amino-5-dimethylhydantoin,



Bailey and Snyder¹ carried out "experiments without result to convert iminoacetonitrile, $\text{NH}(\text{CH}_2\text{CN})_2$, to its ureido derivative in the usual way by the action of potassium cyanate on the hydrochloride of this amine in water solution." On the other hand, "by treatment of iminoacetonitrile in glacial acetic acid with potassium cyanate, saponification of the ureido derivative thus formed, and then esterification," they obtained ethyl hydantoin-1-acetate,



The use of glacial acetic acid as a solvent in effecting the condensation of cyanic acid with benzylidene hydrazones is discussed further on.

A careful survey of the literature has not revealed the use of glacial acetic acid by any previous investigators as a solvent for cyanic acid, although this solvent is frequently used in connection with isocyanates and mustard oils.

Adolf Sonn² has recently announced a valuable method of preparation of substituted ureas, which consists in heating primary amines with urea or mono-substituted ureas in glacial acetic acid solution. He states that "in place of urea, ammonium sulfocyanide can be used," and describes the preparation of diphenyl urea by heating aniline with ammonium sulfocyanide in glacial acetic acid. However, at the time of the publication of Sonn's article, the work described by us had been practically completed.

Ordinarily, the addition of cyanic acid on both primary and secondary amines proceeds smoothly in water solution, and in such cases the use

¹ THIS JOURNAL, 37, 940 (1915).

² Ber., 47, 2437 (1914).

of glacial acetic acid is of course not to be recommended; but it may be that this modification of the urea synthesis will find further application in cases similar to the ones cited above, where the addition of cyanic acid takes place with difficulty, if at all, in water. Furthermore, experiments are being conducted in this laboratory toward an extension of the condensations of cyanic acid with glacial acetic acid as the reacting medium.

As a number of common organic solvents are miscible with glacial acetic acid, experiments were instituted with mixtures of acetic acid with chloroform, benzene, and absolute alcohol as media for effecting the condensation of cyanic acid with ethyl hydrazoisobutyrate. It was found that these substitutes for glacial acetic acid, within certain limits at least, were as effective as the acetic acid itself, so that in all probability the use of these mixed solvents will find application in certain cases where their solvent action is greater than that of the simple glacial acetic acid. Furthermore, in working with ethyl hydrazoisobutyrate, it was found that the addition of cyanic acid takes place in an aqueous acetic acid where the percentage of the acetic acid is above thirty. However, the yield of the desired reaction product is far below that obtained in a medium of glacial acetic acid. It appeared possible that an excess of mineral acid might serve the same purpose as the glacial acetic acid, but it was observed that in aqueous solution, no reaction takes place between cyanic acid and ethyl hydrazoisobutyrate, either when the calculated amount of hydrochloric acid or one mol in excess is employed.

Knorr and Köhler¹ have shown that cyanic acid reacts with hydrazomethane in water solution, forming dimethylsemicarbazide,



which, as far as our information goes, was the first observed instance of a hydrazo compound behaving like a secondary amine towards cyanic acid. Researches carried out in this laboratory² have shown that hydrazo acids readily condense with mustard oils and isocyanates, forming substituted hydantoin; but as a rule hydrazo bodies do not react readily with mustard oils,³ although they react more readily with isocyanates.⁴

As stated above, cyanic acid and ethyl hydrazoisobutyrate react in molecular proportions in glacial acetic acid with the formation of the ethyl ester of 1-isobutyric acid amino-5-dimethylhydantoin. The constitution of this addition product of cyanic acid on ethyl hydrazoisobutyrate was established beyond question by its conversion to 1-amino-5-dimethylhydantoin, and the synthesis of the latter compound from

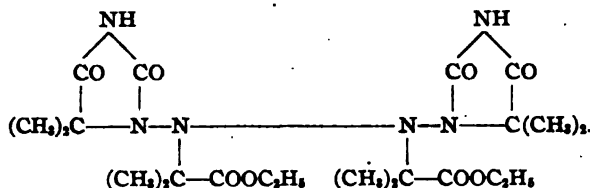
¹ *Ber.*, 39, 3263 (1906).

² *THIS JOURNAL*, 26, 1006 (1904).

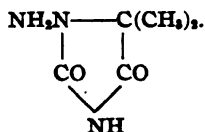
³ *Ber.*, 25, 3115 (1892).

⁴ *Ibid.*, 23, 490 (1890).

hydrazinoisobutyric acid. The ester of the isobutyric acid aminodimethylhydantoin is readily oxidized in the cold, bromine water, for example, giving in quantitative yield a nonvolatile oil, for which we have tentatively assigned the formula

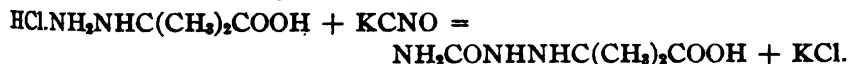


It, furthermore, behaves as a secondary amine toward nitrous acid in the formation of a stable nitroso compound. Heated with sulfuric acid, the isobutyric acid aminohydantoin ester hydrolyzes to 1-amino-5-dimethylhydantoin,



The hydrazine character of the latter substance is shown in its ready condensation with benzaldehyde.

As a definite proof of the constitution of the reaction product of sulfuric acid on the ester of isobutyric acid aminodimethylhydantoin as 1-amino-5-dimethylhydantoin, the synthesis of this substance from hydrazinoisobutyric acid¹ and cyanic acid was attempted. However, here the cyanic acid adds to the β -nitrogen, forming semicarbazinoisobutyric acid,



A similar action of cyanic acid was observed by Darapsky and Berger² in the preparation of ethyl semicarbazinobenzylacetate,



whereas Darapsky and Prabhakar³ found that ethyl hydrazinophenylacetate and cyanic acid give an addition product with the carbonamide rest on the α -nitrogen, of the following constitution:



W. Traube and Hoffa⁴ have made the interesting observation that ethyl hydrazinoacetate yields both of the possible ureido derivatives:



¹ *Ann.*, 290, 17 (1896).

² *Dissertation* (Heidelberg), 1912.

³ *Ber.*, 45, 1658 (1912).

⁴ *Ibid.*, 31, 162 (1898).

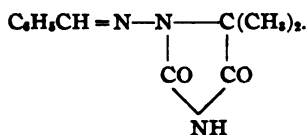
Phenylhydrazine condenses in a similar way with phenyl mustard oil,¹ giving two products of the constitution:



An interesting method of preparing α -ureido derivatives of hydrazino acids, available where they cannot be prepared by the direct action of cyanic acid on the hydrazino acids, is described in the experimental part of this article, which method starts with the addition of cyanic acid on benzylidene hydrazino acids. For example, benzylidene hydrazinoisobutyric acid,



reacts readily in glacial acetic acid with cyanic acid, yielding 1-benzylidene amino-5-dimethylhydantoin,



Attempts to effect this reaction in aqueous solution failed. The benzylidene compound of the aminodimethylhydantoin can be easily hydrolyzed, forming the corresponding aminodimethylhydantoin, identical with the reaction product of sulfuric acid on the ethyl ester of 1-isobutyric acid amino-5-dimethylhydantoin. Busch and Walter³ employed a method similar to the one followed above to obtain α -phenylsemicarbazide,



from benzylidene phenylhydrazine,



However, the intermediary benzylidene- α -phenylsemicarbazide, according to our observations, cannot be prepared by the modified Wöhler synthesis used by us in the case of benzylidene compounds of hydrazino acids. Busch obtained his ureido compound by treating benzylidene phenylhydrazine with carbonyl chloride, and the resulting benzylidene phenylhydrazinecarboxylic acid chloride,



¹ *Ber.*, 34, 321 (1901).

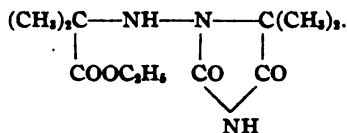
² By J. R. Bailey and L. A. Mikeska: The benzylidenehydrazinoisobutyric acid used in the above experiment was obtained by treating a hydrazine solution with one mol of acetone, adding sodium bisulfite on the resulting hydrazone (*Ber.*, 37, 4073 (1904); *THIS JOURNAL*, 37, 936 (1915)) replacement of the sulfonic acid rest by the CN group, saponification of the resulting nitrile, and treatment of the hydrazino acid thus formed with benzaldehyde. This method of preparation of benzylidene hydrazinoisobutyric acid, and consequently of hydrazinoisobutyric acid itself, is to be preferred in point of simplicity to the method of Thiele and Heuser (*Ann.*, 290, 15 (1896)) where, although the yields are excellent, the procedure is complicated by the number of steps involved and the time required for their completion.

³ *Ber.*, 36, 1359 (1903).

with ammonia. Attention is directed to the fact that the cyanic acid reaction with the benzylidene compounds of hydrazino acids, apart from its preparative value, may be used to characterize hydrazino acids.

Experimental Part.

Preparation of the Ethyl Ester of 1-Isobutyric Acid Amino-5-Dimethylhydantoin,



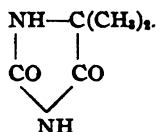
—35 g. of ethyl hydrazoisobutyrate, prepared according to the method of Thiele and Heuser,¹ are dissolved in 70 cc. of glacial acetic acid, and then a slight excess of solid potassium cyanate, 18 g., added in small portions during an interval of forty-five minutes, the temperature being kept below 40°. The reaction at first proceeds without gas evolution; but at the end of one hour the temperature of 60° is maintained in the solution for thirty minutes, during which time there is some gas evolved. Potassium cyanate, when dissolved in pure glacial acetic acid, gives off carbon dioxide quite vigorously, even when the temperature is kept below 40°. To isolate the reaction product, the acetic acid solution is diluted to three times its volume, and the acid neutralized with ammonia, while the container is immersed in ice-water. The larger part of the hydantoin compound crystallizes out, and a further small amount can be obtained by extraction with chloroform. The yield is about 86% of the theoretical. The new substance is readily soluble in the common organic solvents, petroleic ether excepted. For analysis it was crystallized from a benzene-petroleic ether mixture, and finally from 50% alcohol. From the latter solvent it can be obtained in plates resembling rhombic prisms. The substance melts at 104–105°. It does not dissolve in dilute mineral acids in the cold, but slowly dissolves in 50% sulfuric acid on heating with the elimination of the isobutyric acid rest. Even in the cold it reduces bromine water instantaneously and permanganate slowly. In the preparation of the above isobutyric acid aminodimethylhydantoin ester it is possible within certain limits to use mixtures of glacial acetic acid with various organic solvents without materially affecting the yield, and it was further observed that the reaction also takes place in aqueous acetic acid of a concentration above 30%, but with diminished yield depending, no doubt, on the amount of water present. Our attempts to condense hydrazoisobutyric acid itself, as well as the corresponding nitrile, with cyanic acid by the method employed above for the ester were unsuccessful.

¹ Ann., 290, 29 (1896).

Calc. for $C_{11}H_{19}O_4N_3$: C, 51.36; H, 7.39; N, 16.34.

Found: C, 51.46; H, 7.59; N, 16.63.

Oxidation Product of the Ethyl Ester of Isobutyric Acid Aminodimethylhydantoin with Bromine.—The oxidation can be carried out either in a dilute alcohol solution or in 50% acetic acid. In one experiment 7 g. of the hydantoin compound were dissolved in 20 cc. of glacial acetic acid and in the course of the oxidation a total of 20 cc. of water added. It was found convenient to aspirate the bromine into the acetic acid until it imparted for five minutes a deep yellow color to the solution. The excess of bromine was then discharged by leading in sulfurous acid gas. The acid was next neutralized with ammonia, whereupon an oil separated and a further amount was obtained by shaking out the aqueous layer with ether. This oil decomposes at about 150° *in vacuo* with steady gas evolution and with the sublimation of a beautifully crystallizing white solid, probably acetonylurea,

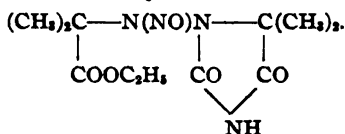


—The oil, dissolved in absolute alcohol, separates out a white crystalline substance on the addition of sodium alcoholate. For analysis a sample of the oil in ether was dried with potassium carbonate, and the ether removed at 60° *in vacuo*. This oil, which has a specific gravity 1.0524, is probably the ethyl ester of bis-1-isobutyric acid amino-5-dimethylhydantoin. However, the product has so far not been prepared sufficiently pure to furnish a conclusive analysis.

Calc. for $C_{22}H_{30}O_8N_4$: C, 51.56; H, 7.03; N, 16.41.

Found: C, 49.71; H, 8.09; N, 17.98.

Ethyl Ester of Nitroso-1-Isobutyric Acid Amino-5-Dimethylhydantoin,



—The hydantoin ester is dissolved in glacial acetic acid, the solution cooled in ice-water, and one and a half mols of solid sodium nitrite stirred in. After the reaction is complete, the acetic acid is neutralized with ammonia, whereupon the nitroso derivative precipitates. Its solubilities are similar to those of the mother substance. From water it crystallizes in laminae of thin plates of a faint yellow color, which melt undecomposed at 104° . The substance gives the Liebermann reaction.

Calc. for $C_{11}H_{19}O_5N_4$: C, 46.15; H, 6.29; N, 19.58.

Found: C, 46.05; H, 6.44; N, 19.84.

Nitroso-1-isobutyric Acid Amino-5-Dimethylhydantoin.—The nitroso ester described above is warmed for thirty minutes with a slight excess of strong potassium hydroxide solution. On neutralizing with hydrochloric acid under cooling, the nitroso acid separates out. It is soluble in alcohol, acetic ether, ether, and water, crystallizing from the latter solvent in minute rhombic plates, which melt at 165° with decomposition.

Calc. for $C_8H_{14}O_5N_4$: C, 41.86; H, 5.43; N, 21.71.

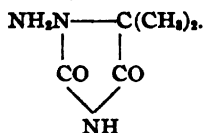
Found: C, 41.80; H, 5.72; N, 21.73.

1-Isobutyric Acid Amino-5-Dimethylhydantoin.—The hydantoin ester is readily saponified by treatment with a slight excess of strong potassium hydroxide solution for fifteen minutes at water-bath temperature. On acidifying with hydrochloric acid, the hydantoin acid crystallizes out. It is readily soluble in alcohol, acetic ether and hot water, moderately soluble in chloroform and ether, and difficultly soluble in benzene. Purified from water, the acid is obtained in long, slender, prismatic plates, melting at 192.5° undecomposed. Above 200° it decomposes with gas evolution, and on cooling remains viscous.

Calc. for $C_8H_{12}O_4N_2$: C, 47.16; H, 6.55; N, 18.34.

Found: C, 46.96; H, 6.62; N, 18.55.

1-Amino-5-Dimethylhydantoin,

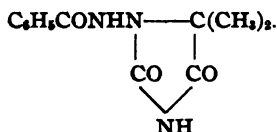


—6 g. of the hydantoin ester are put into 30 cc. of 50% sulfuric acid, and the mixture heated in an oil bath at 110° for four hours after complete solution has been effected. The reaction is attended with a vigorous gas evolution. For the isolation of the aminohydantoin, the sulfuric acid is carefully poured into an excess of ammonium hydroxide with cooling, the solution evaporated to dryness *in vacuo*, and the residue extracted with acetic ether. This hydrazine is readily soluble in water and the common organic solvents, petroleic ether excepted. Purified by crystallization from benzene and then from acetic ether, it is obtained in long, slender prisms, melting undecomposed at 170° . It readily forms a benzoyl and a benzylidene derivative. The hydrazine reduces bromine water, permanganate and mercuric oxide in the cold and there separates in extremely poor yield a small amount of an oxidation product, the investigation of which will be taken up later. It is to be expected that conditions will be established here for obtaining the oxidation product, which is probably a tetrazene, in satisfactory yield.¹

¹ THIS JOURNAL, 30, 1412 (1908).

Calc. for $C_8H_7O_2N_2$: C, 41.96; H, 6.29; N, 29.37.
 Found: C, 41.98; H, 6.38; N, 29.61.

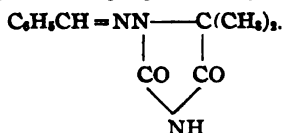
1-Benzoylamino-5-Dimethylhydantoin,



—One gram of the aminohydantoin is boiled with one mol of benzoyl chloride in acetic ether solution for one hour. Reaction takes place readily and one-half of the aminohydantoin separates as the hydrochloride. This salt was not analyzed. After filtration, the acetic ether solution is evaporated to dryness, any benzoic acid removed by extraction with ether, and the residue crystallized from water. Thus purified it melts at 241° to a clear liquid undecomposed.

Calc. for $C_{12}H_{11}O_2N_2$: N, 17.00.
 Found: N, 17.02.

1-Benzylideneamino-5-Dimethylhydantoin,



—The benzylidene compound separates in quantitative yield on shaking an aqueous solution of the aminohydantoin with the calculated amount of benzaldehyde. By recrystallization from alcohol it can be obtained in long needles, melting undecomposed at $191-192^\circ$. The substance is readily soluble in ether, benzene and chloroform, and almost insoluble in water.

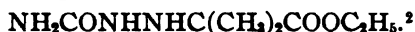
Calc. for $C_{15}H_{15}O_2N_2$: C, 62.34; H, 5.63; N, 18.18.
 Found: C, 62.43; H, 5.78; N, 18.45.

The above hydrazone can also be prepared by condensing cyanic acid with benzylidene hydrazinoisobutyric acid¹ as follows: The latter sub-

¹ *Preparation of Benzylidene Hydrazinoisobutyric Acid.*—20 g. of hydrazine sulfate in 50 cc. of water are converted to the acid salt $(NH_2NH_2)_2H_2SO_4$ by the addition of 21.2 g. of potassium carbonate. 17.8 g., one mol, of acetone are next added under cooling, and this solution is then treated with a concentrated solution of one mol of sodium acid sulfite. After standing two hours 10 g. of potassium cyanide, one mol, is added to the solution, whereupon a supernatant layer of oil separates. In order to convert the hydrazinoisobutyronitrile, $NH_2NHC(CH_3)_2CN$, to its amide, the mixture is allowed to stand twenty-four hours with twice its volume of concentrated hydrochloric acid, and saponification finally effected by boiling the solution for one hour. The excess of mineral acid is removed by distillation *in vacuo*, the residue taken up with a little water, an excess of sodium acetate added, and the solution treated in the usual way with benzaldehyde. In this way a mixture of benzylidene hydrazinoisobutyric acid and benzalazine is obtained. The method of Thiele and Heuser (*Ann.*, 290, 16

stance in glacial acetic acid is treated with potassium cyanate by the method described above in the preparation of the ethyl ester of 1-isobutyric acid amino-5-dimethylhydantoin. The reaction mixture is allowed to stand twelve hours, and is then diluted to eight times its volume, whereupon the difficultly soluble 1-benzylidene amino-5-dimethylhydantoin separates. Working with 5 g. of benzylidene hydrazinoisobutyric acid in 50 cc. of glacial acetic acid, 4.6 g. of the condensation product were obtained, and this proved identical with the product described in the foregoing preparation. The benzylidene compound thus obtained for further confirmation of its constitution was submitted to steam distillation in the presence of one mol of sulfuric acid. Benzaldehyde collected in the receiver and 1-amino-5-dimethylhydantoin was isolated from the solution in the distillation flask by the method employed above in the preparation of this substance. All attempts to condense cyanic acid with benzylidene hydrazinoisobutyric acid in water solution failed.

Action of Potassium Cyanate on the Hydrochloride of Ethyl Hydrazinoisobutyrate.—To 2.9 g. of ethyl hydrazinoisobutyrate, prepared according to the method of Thiele and Heuser,¹ was added the calculated amount of hydrochloric acid, and then 1.8 g. of potassium cyanate. After standing overnight, the solution did not react with benzaldehyde, a proof that no aminodimethylhydantoin is formed. Extraction with chloroform yielded a product that proved to be ethyl semicarbazinoisobutyrate,



As further confirmation, a nitrogen determination was made.

Calc. for $\text{C}_7\text{H}_{14}\text{O}_4\text{N}_2$: N, 22.22. Found: N, 22.13.

AUSTIN, TEXAS.

THE VAPOR PRESSURE OF ETHANE AND ETHYLENE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS¹

BY G. A. BURRELL AND I. W. ROBERTSON.

Received June 3, 1915.

The authors of this report have needed at various times, in working on the condensation of the constituents in natural gas, and in studying the separation of gas mixtures by fractionally distilling them, certain

(1896)) may be used to remove the benzalazine. Stir the mixture of benzaldehyde compounds with a little dilute ammonia, and after the benzylidene hydrazinoisobutyric acid has completely dissolved, filter from the undissolved benzalazine. Finally extract the last traces of benzalazine from the ammonia solution with ether and then precipitate the benzylidene hydrazino acid by neutralizing with dilute acetic acid. The yield obtained was about 42% of the theoretical (Bailey and Mikeska).

¹ *Loc. cit.*

² *Am. Chem. J.*, 28, 386 (1902).

³ Published by permission of the Director of the Bureau of Mines.

vapor-pressure measurements of gases at low temperatures. These have not been determined in the case of ethylene, and only for a limited range (20° below the normal boiling point) in the case of ethane. Hence in this paper are shown observations from 760 mm. down to 1 mm. Vapor pressures of propane, propylene, *N*-butane, iso-butane, butylene and acetylene will follow in subsequent articles.

Experimental.

The apparatus with which the work was performed is shown at Figs. 1 and 2. Referring to Fig. 1: The gas whose vapor pressure was measured was confined in the glass bulb *b*. The latter communicated on one side with a manometer and on the other side with a Töpler pump. The bath liquid was confined in a Dewar flask about 35 cm. high and 10 cm. wide inside measurements. It was not silvered, hence temperatures on pentane

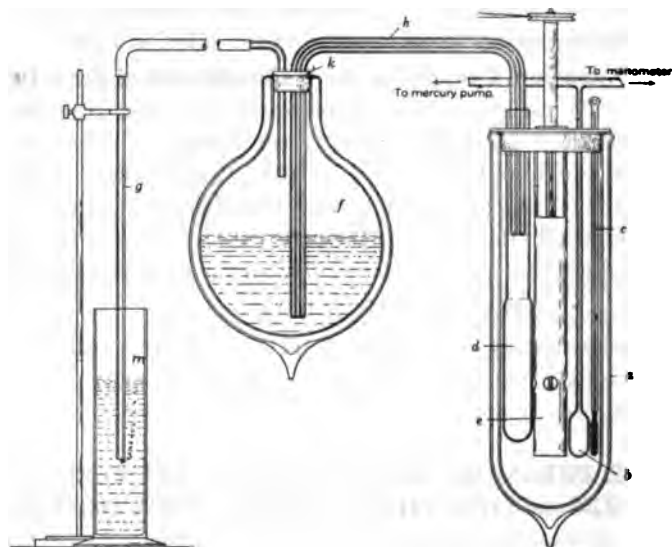


Fig. 1.—Vapor-pressure apparatus and cooling arrangement.

thermometers could be observed through its walls. *e* is a circulator pump operated by a small electric motor. The bath liquid (natural gasoline) was drawn into the pump at the base and discharged through four holes in the casing. By this means vigorous and efficient stirring was accomplished. *c* is a pentane thermometer for registering temperatures. *d* is a glass test-tube open at the top into which liquid air was forced from the Dewar flask through the tube *h*, for the purpose of cooling the bath. This arrangement of cooling and maintaining constant temperatures was devised by Henning.¹ The tube *h* is double-walled and evacuated. At one end it passes through the two-hole stopper *k* and dips

¹ F. Henning, *Z. Instrumentikunde*, 33, 33 (1913).

beneath the surface of the liquid air in *f*. Another glass tube is shown passing through the stopper *k*. It was not immersed in liquid air. A rubber tube joined it to *g*. The latter is shown dipping beneath a cylinder of water, *m*. By lowering or raising *g* more or less pressure was exerted in *f* and varying quantities of liquid air could be forced through *h* into *d*. The depth of immersion of the tube *g* could be so regulated that just enough liquid air could be forced into *d* to compensate for the heat absorption of the bath, thereby maintaining the temperature of the bath constant within 0.04° , although temperatures could not be determined with that degree of precision. However, close to the normal boiling point of ethane, the temperature changes about 4° for each 100 mm., or 0.04° per mm., and no trouble was experienced in maintaining pressures constant to 1 mm., close to the boiling point of ethane (or ethylene) for as long as 15 minutes, the maximum length of time the bath was kept constant at one observation. By constantly dropping a little water into the glass cylinder *m*, to keep the water level therein always at the same height above the liquid-air level in *f*,¹ constant temperatures could be maintained as long as the liquid air lasted. The bath liquid was casing-head gasoline obtained at a "plant" where gasoline is extracted from natural gas by subjecting it to a pressure of 250 lbs. per square inch and cooling, at ordinary temperatures. This condensate contained a large proportion of the liquid butanes and propane, besides some of the ordinary gasoline constituents, the pentanes, hexanes, etc., and did not jelly when the lighter portions were used, until a temperature of -175° was reached.²

Two views of the manometer are shown at Fig. 2. In some respects it is similar to one described by Germann.³

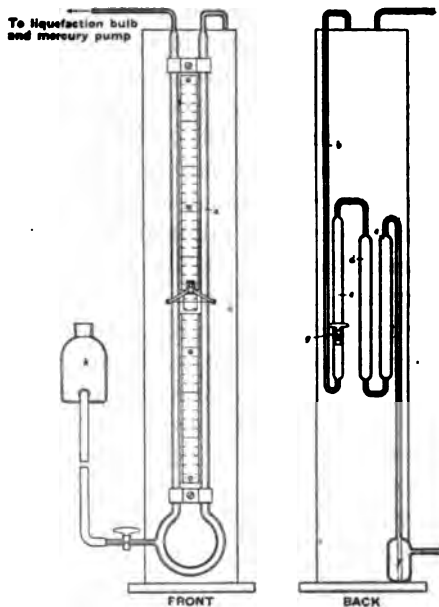


Fig. 2.—Mercury manometer.

¹ As the liquid air in *f* evaporates its level changes, and hence the difference in height between its level and the water level in *m* changes.

² A steel tank such as is used for confining gases under heavy pressure was shipped to the natural-gas-gasoline plant of the Bessemer Gas Engine Co. at Follansbee, W. Va., where it was filled under pressure with the gasoline.

³ A. F. O. Germann, "A modified precision barometer," *THIS JOURNAL*, 36, 2456, 2459 (1914).

The glass parts were thoroughly cleaned and dried and purified mercury¹ poured into the leveling bottle *h*. The latter was then raised high enough to force mercury into the capillary *b* and reservoir *c*. Next, *h* was lowered, whereupon the mercury column fell, leaving a mercury seal in *b* and *c* and a vacuum above the column in *a*. The precaution recommended by Germann to clear the space above the mercury of traces of air was followed out as follows: Several days after the filling of the manometer, a water pump was attached to the mercury trap *f* and the trace of air that had accumulated in *a* removed. *d* and *e* were filled with soda lime. The scale of the manometer was made of steel, and graduated in 0.5 mm. It was checked against a cathetometer² with a rod of carefully ground steel, carrying a scale divided into millimeters and fitted with a vernier to read to 0.1 mm. It was also checked against a precision barometer owned by the Bureau of Mines.

Preparation of Gases.—Ethylene was prepared by heating sulfuric acid and ethyl alcohol together at a temperature of 165°. The evolved gases were passed through caustic potash and phosphorus pentoxide. Next they were fractionated at the temperature of liquid air, and air, together with any carbon monoxide or hydrogen formed in the reaction, was withdrawn with a Töpler pump.³ Fractionation at this temperature was repeated until no more gas was removed by the pump. The gas was further fractionated at a temperature not higher than -140°. At this temperature ethylene was withdrawn by means of the pump, and traces of water vapor or other gases of much higher boiling point than ethylene remained frozen. In addition to this preliminary purification, the gas was cooled at the temperature of liquid air after it had been introduced into the vapor-pressure apparatus and the apparatus evacuated to make sure that air had not been trapped in the transfer. As a further check on the purity of the gas, portions of it were allowed to boil off during the vapor-pressure measurements, which were repeated with the remaining portions. In addition, pressure observations were made with both a rising and a falling mercury level in the manometer.

Ethane was prepared by the electrolysis of a saturated solution of sodium acetate, and purified in essentially the same manner as the ethylene.

Temperature Measurements.—It was originally intended to measure temperatures with a platinum resistance thermometer, but so much delay was experienced in obtaining the necessary equipment that it was decided to perform the work with a pentane thermometer. With this thermometer temperatures as low as -195° could be measured. The scale divisions

¹ Purified by the method of Hulett, *Phys. Rev.*, 34, 307 (1911).

² This cathetometer is described by Wm. Gaertner & Co., their catalog M-L, No. M-902.

³ See THIS JOURNAL, 36, 1537 (1914); also *J. Ind. Eng. Chem.*, 7, 17 (1915).

were 1° , but were so widely spaced that two different observers could easily make readings at a particular temperature which checked to 0.2° , and in most cases to 0.1° .

Holborn,¹ who devised the pentane thermometer, found that it followed the fluctuations of a hydrogen thermometer, in most cases to 0.1° , if properly used.

Calibration of Thermometers.—The authors calibrated their pentane thermometers against certain fixed points established by F. Henning.² This scale, together with observations by others, follows. With the exception of Siemens's³ values, the data given were all cited by Henning.

BOILING AND MELTING POINTS OF DIFFERENT SUBSTANCES BY DIFFERENT OBSERVERS.

	Henning.	Timmermans.	Baly.	Dewar.	Travers.	Onnes.	Siemens.
Oxygen (b. p.) 760 mm.	—183.01		—181.9	—182.5	—182.8	—182.99	—182.99
Oxygen (b. p.) 740 mm.	—183.27						
Carbon dioxide (b. p.)..	—78.52						—78.44
Mercury (m. p.).....	—38.89	—38.6					—38.77
Ethyl ether (m. p.)....	—123.6	—123.3					
Carbon bisulfide (m. p.)	—112.0	—111.6					—112.16
Chloroform (m. p.).....	—63.7	—63.3					
Chlorobenzol (m. p.)....	—45.5	—45.0					
Nitrogen (b. p.).....							—195.84

It will be observed that Henning, Onnes and Siemens agree fairly well. For the boiling point of oxygen the agreement is striking, the variation being only 0.02° , which is the utmost precision obtainable with the hydrogen thermometer.

The pentane thermometers used by the authors were calibrated at four points: the normal boiling point of carbon dioxide, the melting points of carbon bisulfide and ethyl ether, and at -183.27° (the temperature of liquid oxygen boiling at 740 mm.). The carbon dioxide was prepared in two ways: first, by using that furnished commercially in steel tanks, after thoroughly fractionating it at low temperatures and passing it over phosphorus pentoxide to remove water vapor; and, second, by the action of dilute sulfuric acid on potassium bicarbonate. It also was thoroughly purified in the same way as the carbon dioxide obtained from the commercial tanks. The ethyl ether and carbon disulfide were the purest reagents commercially obtainable. No difference was found in their melting points after redistilling them over phosphorus pentoxide.

The oxygen was prepared by heating potassium permanganate in an evacuated hard-glass tube, discarding the first portions of gas that came off, then liquefying the remainder with liquid air, and pumping it into

¹ *Ann. Phys.*, 6, 242 (1901).

² *Ibid.*, 43, 294 (1913).

³ H. V. Siemens, *Ibid.*, 42, 871–878 (1913).

another container. When calibrating against the vapor pressure of liquid oxygen, liquid oxygen was used for the temperature bath.

The following table shows the observations as made with the different pentane thermometers. They are uncorrected readings and show how the thermometers varied among themselves. For instance, at the normal boiling point of carbon dioxide, thermometer No. 8161 read -77.8° , thermometer No. 707 read -81.8° , and thermometer 504 read -78.8° .

TEMPERATURE OBSERVATIONS WITH DIFFERENT PENTANE THERMOMETERS.

Therm. No.	CO ₂ (from tank), b. p. mm.	CO ₂ (from K ₂ CO ₃), b. p. mm.	CS ₂ , m. p.		Ethyl ether, m. p.		O ₂ , b. p. mm.
8161	-77.8	-77.7	-111.0	-111.0	-122.8	-122.8	
707	-81.8	-81.9	-114.0	-114.0	-125.5	-122.5	-182.0
507	-78.8	-78.6	-111.6	-111.6	-123.5	-123.5	-183.0

In making independent observations of the vapor pressures of both ethylene and ethane with different thermometers (as noted later) and then correcting them according to their respective calibrations, it was found that the same results were obtained with the different thermometers, thus showing that the thermometers did not vary seriously (at uncali-

brated points) from a straight line drawn between calibrated points.

There are shown in Tables I and II saturated vapor-pressure measurements for ethane and ethylene, also the plotted curves (Fig. 3) for the values as found.

Near the normal boiling points a very small temperature change is represented by large pressure change. For instance, in the case of ethane, 1.6° ($90.9-89.3^{\circ}$) = 60 mm. Therefore, 0.2 (the limit of our thermometrical accuracy) corresponds to 7.5 mm.

In the case of ethylene, 0.2° corresponds to about 7 mm. at the normal boiling point. In the case

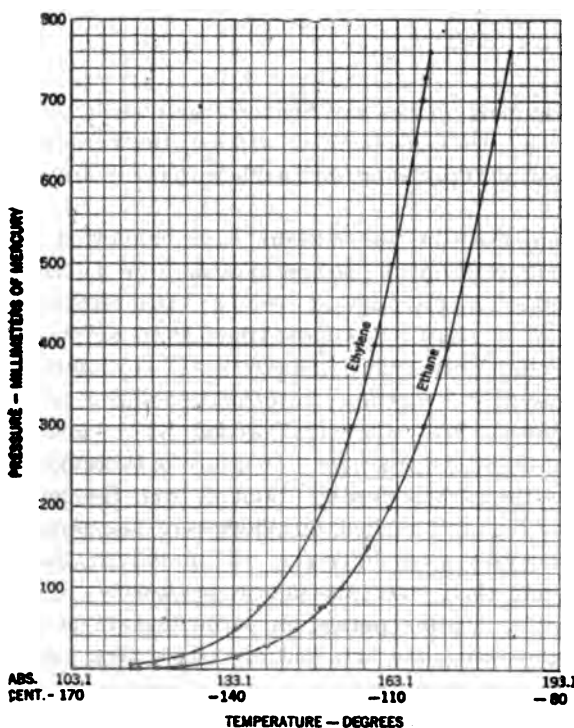


Fig. 3.—Curves showing absolute temperatures plotted against pressures in mm. of mercury.

of ethane 0.2° corresponds to almost 1 mm. between -128.5° and -133.7° and at the lowest temperatures given (-157.7° and -159.8°) 1 mm. = 2.1° or $0.2^{\circ} = 0.09$ mm.

TABLE I.—SATURATED VAPOR PRESSURES OF ETHYLENE AT TEMPERATURES BELOW THE NORMAL BOILING POINT.

Thermom- eter 707.	Thermom- eter 8161.	Thermom- eter 504.	Average temperature °C.	Average tempera- ture °Abs. ¹	Observed pressure, mm.	Calculated pressure, mm.
-103.7	-103.9	-104	-103.9	169.2	760	760
-104.8		-104.9	-104.8	168.3	730	726
-105.3	-105.4	-105.5	-105.4	167.7	700	701
-106.8	-106.8		-106.8	166.3	650	643
-107.9	-108.0	-108.2	-108.0	165.1	600	595
-111.0	-111.0		-111.0	162.1	500	512
-114.1	-114.1		-114.1	159.0	400	400
-118.2	-118.1		-118.2	154.9	300	300
-123.5	-123.7		-123.6	149.5	200	200
-132.0		-132.3	-132.2	140.9	100	98
-135.2		-135.3	-135.3	137.8	75	74
-139.5		-139.7	-139.6	133.5	50	49
-144.2		-144.4	-144.3	128.8	31	30
-149.3		-149.6	-149.4	123.7	17	17
-154.7		-154.9	-154.8	118.3	9	9
-159.8		-160.0	-159.9	113.2	4	4

¹ Ice point on the absolute scale is 273.1° . Equation of the curve is $\log P = -762.52/T + 1.75 \log T - 0.00532 T + 4.3910$.

TABLE II.—SATURATED VAPOR PRESSURES OF ETHANE AT TEMPERATURES BELOW THE NORMAL BOILING POINT.

Thermom- eter 707.	Thermom- eter 8161.	Thermom- eter 504.	Average temperature °C.	Average tempera- ture °Abs.	Observed pressure, mm.	Calculated pressure, mm.
-89.3	-89.4		-89.3	183.8	760	760
-90.8	-90.9		-90.9	182.2	700	711
-92.2	-92.3		-92.3	180.8	650	651
-93.7	-93.7		-93.7	179.4	600	604
-97.0	-96.8		-96.9	176.2	500	495
-100.4	-100.5	-100.6	-100.5	172.6	400	410
-105.2	-105.0	-105.1	-105.1	168.0	300	307
-111.4	-111.2	-111.3	-111.3	161.8	200	200
-115.3		-115.4	-115.3	157.8	150	149
-120.3	-120.1	-120.2	-120.2	152.9	100	100
-123.1		-123.2	-123.2	149.9	77	77
-124.0		-124.2	-124.1	149.0	74	73
-128.4		-128.7	-128.5	144.6	49	47
-133.6		-133.9	-133.7	139.4	29	28
-138.9		-139.2	-139	134.1	15	15
-149.4		-149.7	-149.5	123.6	4	4
-154.6		-154.7	-154.6	118.5	3	2
-157.7		-157.8	-157.7	115.4	2	1.2
-159.8		-159.9	-159.8	113.4	1	0.8

Equation of the curve is $\log P = -1050.85/T + 1.75 \log T - 0.01342T + 7.10217$.

Since the accuracy of thermometer readings was 0.2° and of pressure readings 1 mm., the observations at the higher temperatures were made by adjusting the thermostat until the mercury in the manometer remained constant to 1 mm. Then the thermometer was read. In the case of ethane at the lower temperatures (below -128.5°) the thermostat was adjusted until the pentane thread in the thermometer remained constant to 0.2° . Next the pressure was read. The same procedure was followed in the case of ethylene, the object being to remain within the experimental error, at all times, in reading temperatures and pressures.

Calculation of the Curves of the Vapor Pressure.

This may be done with the aid of the approximate and empirical formula of Nernst:¹

$$\log P = -\frac{\lambda_0}{4.571T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C$$

in which the constants λ_0 , ϵ , and C may be found by taking values of P at three different temperatures. In the case of ethane, taking as the values of P at three different temperatures the following, 760 mm., 183.8° Abs.; 200 mm., 161.8° ; 4 mm., 123.6° ; the equation of the curve becomes:

$$\log P = -\frac{1050.85}{T} + 1.75 \log T - 0.01342T + 7.10217.$$

In the case of ethylene, taking as the values of P at three different temperatures the following, 700 mm., 167.7° Abs.; 300 mm., 154.9° ; 17 mm., 123.7° ; the equation of the curve becomes:

$$\log P = -\frac{762.52}{T} + 1.75 \log T - 0.00532T + 4.39100.$$

From these equations one can calculate the vapor pressure of ethane and ethylene at any temperature. This has been done as shown in Tables I and II. It will be noted that in the case of ethylene there is one discrepancy outside the error of experimentation, 12 mm. (the -111° point) corresponding to 0.65° . In the case of ethane, 11 mm. (the -90.9° point) corresponds to 0.3° ; 10 mm. (the -100.5° point) corresponds to 0.4° ; and 7 mm. (the -105.1° point) corresponds to 0.3° . The agreement is not as good as in the case of ethylene.

The results may also be expressed by plotting the common logarithm of the pressure against the reciprocal of the absolute temperature (Fig. 4). The results lie on a straight line. The straight lines were drawn by obtaining an equation from the average of all the results computed by the method of least squares and drawing the lines according to these equations. For ethylene the equation is:

¹ "Theoretical Chemistry," 1911, p. 719.

$$\text{Log } P = -\frac{767.8}{t} + 7.433 \quad (1)$$

For ethane:

$$\text{Log } P = -\frac{831.4}{t} + 7.42 \quad (2)$$

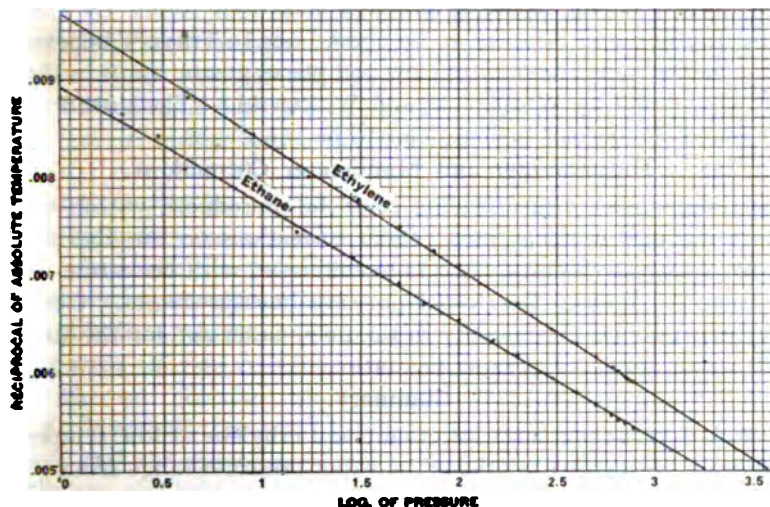


Fig. 4.—Curve showing common logarithm of vapor pressure plotted as a function of the reciprocal of the absolute temperature.

Heats of Evaporation of Ethane and Ethylene.

The heats of evaporation of ethane and ethylene for the temperature range studied may be calculated from the Clausius-Clapeyron equation:

$$Q = \frac{(d \ln p) RT^2}{dT} \quad (3)$$

in which Q is the heat of evaporation in calories per gram molecule, $\ln p$ is the natural logarithm of the vapor pressure, T the absolute temperature, and R the gas constant (1.985).

Integrating Equation 3 and assuming that Q is a constant (which is permissible, however, only for a limited temperature range), one obtains:

$$\ln p = -\frac{Q}{RT} + \text{const.}$$

The values 767.8 and 831.4 in Equations 1 and 2 represent the average of all the determined points on the curve.

Using these values in the Clausius-Clapeyron equation, and changing from common to natural logarithms one finds in the case of ethylene:

$$Q = R(767.8 \times 4.571) = 3510 \text{ calories}$$

and in the case of ethane:

$$Q = R(831.4 \times 4.571) = 3800 \text{ calories}$$

The only other vapor-pressure values at low temperatures for ethane or ethylene (aside from normal boiling points) are those of Maas and McIntosh,¹ who worked out values for ethane from -88.5° (the normal boiling point found by them) to -107.8° . At this temperature they found a pressure of 287 mm., or 2.3° from the value the authors found at 287 mm.

The normal boiling point of ethylene has been found by Olszeswki and by Ramsey and Travers to be 170.5° abs.² Travers believes both of these values to be about 1° too low and places greater faith in the value 169.5° abs. found by Wroblewski and Witkowski.³ The authors of this paper found the normal boiling point to be 169.2° abs.

Thermometer and Manometer Corrections.

The thermometer measurements could be reproduced within 0.2° and pressure readings within 1 mm. Stem corrections on the thermometers were not necessary because they were calibrated with the same depth of immersion as during the vapor-pressure measurements. Corrections for the expansion of the mercury in the manometer and for the steel scale, all fell within the error of experimentation.

Summary.

Saturated vapor pressures for ethane and ethylene at low temperatures are shown. In the case of ethane the vapor pressures range from 760 mm. at -89.3° to 1 mm. at -159.8° . In the case of ethylene the vapor pressures range from 760 mm. at -103.9° to 4 mm. at -159.9° .

The authors' experience with a bath devised by Henning for maintaining constant low temperatures is described.

Valuable assistance in conducting this work was furnished by Dr. G. A. Hulett, consulting chemist, F. M. Seibert, assistant chemist, and Dr. J. K. Clement, physicist, of the Bureau of Mines.

CHEMICAL LABORATORY, BUREAU OF MINES,
PITTSBURGH, PA.

ON THE REACTIONS OF BOTH THE IONS AND THE MOLECULES OF ACIDS, BASES AND SALTS.

THE REACTIONS OF SODIUM ETHYLATE WITH METHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25° .⁴

[TWENTY-FIRST⁵ COMMUNICATION ON CATALYSIS.]

BY H. C. ROBERTSON, JR., AND S. F. ACREE.

Received April 15, 1915.

When Brunel and Acree began, in March, 1905, work on the theory that *both the ions and the nonionized form of acids, bases and salts must be considered*

¹ O. Maas and McIntosh, *THIS JOURNAL*, 36, 737 (1914).

² M. W. Travers, "The Experimental Study of Gases," p. 243 (1901).

³ *Loc. cit.*

⁴ We are indebted to the Carnegie Institution of Washington for aid in this work.

⁵ For references see *Am. Chem. J.*, 49, 474 (1913).

chemically active, the reactions of alkyl halides with the urazole salts¹ and acids were chosen as a very important class of compounds with which to work out the above theory and our hypothesis of tautomeric² salts. It was seen that work with different³ salts and different alkyl halides would be necessary in order to secure definite proof that the alkyl halide reacts with both the anion and the molecule of the electrolyte, and to learn the influence of different groups, and the position of the metal in the periodic system, on these reaction velocities. In every case studied since that time we have found both the anions and nonionized electrolytes taking part in the transformations according to the equation $K_m = [K_i\alpha + K_m(1 - \alpha)][1 + fC \text{ salt}]$.

The most convincing argument in favor of the theory that both the ions and molecules react with the alkyl halides lies in the fact that the ethylate (phenolate) ion common to sodium, potassium and lithium ethylates (phenolates) should and does react with the *same*⁴ velocity with the *same* alkyl halide, whereas the nonionized forms of these salts are *different* and react with *different* velocities with the same alkyl halide, in accordance with the theory. To illustrate, it was shown in the preceding article by Dr. E. K. Marshall that ethyl bromide and ethyl iodide react with both the anion and the nonionized form of sodium ethylate, and that potassium ethylate and lithium ethylate also react with these two alkyl halides in entire accordance with the theory.

In order to make the evidence for the theory as broad as possible we began in 1909 the present study of the action of methyl iodide on sodium ethylate at 25°. The work on methyl iodide and potassium and lithium ethylates at 25° was finished in 1912-13 by Dr. J. H. Shrader and Dr. Julia Peachy Harrison, and gave still further evidence for the usefulness of the hypothesis. Practically the *same* value for K_i was found for all three salts, but *different* values were obtained for K_m for the *different* nonionized forms of the salts, as is shown in the following table:

	K_i	K_m
Dr. H. C. Robertson: sodium ethylate and methyl iodide.....	0.127	0.0594
Dr. Bessie Marion Brown: the same.....	0.1285	0.0581
Dr. J. H. Shrader: lithium ethylate and methyl iodide.....	0.1367	0.03871
Dr. Julia Peachy Harrison: potassium ethylate and methyl iodide..	0.1259	0.0687

Salt Catalysis.⁵

We recognize that the K_i and K_m calculated here may involve another reaction, called at present a "salt effect," for which a correction must be

¹ *Am. Chem. J.*, 37, 71 (1907); 43, 505 (1910); 44, 219 (1910).

² *Ibid.*, 49, 116 (1913).

³ *Ibid.*, 39, 229 (1908).

⁴ *Ibid.*, 48, 356, 378 (1912); 49, 484 (1913).

⁵ For the literature on "salt catalysis" see *Ibid.*, 49, 350, 485 (1913), and other recent papers.

made later. In order to learn the effect of such a "salt effect" on the values of K_i and K_m , we have assumed a case in which we have corrected, in Table XXIII, the observed values of K_N for a positive "salt catalysis" of 8% per gram molecule of electrolyte. It is seen in Table XXIV that this positive catalysis of 8% raises K_i from 0.127 to 0.136, about 7%, and lowers K_m from 0.0594 to 0.05538, a little less than 7%. It is evident from the harmony of our data with the results of Dr. Shrader and Dr. Harrison that we must conclude at present that the "salt effect," whether large or small, is nearly the same for the sodium, potassium and lithium ethylates. When we collect our final data we shall be able to discuss this subject much more fully.

Experimental.

The methods used have been described fully in earlier papers.¹ The values of A, B and α are given in terms of the number of cc. of acid necessary to neutralize 10 cc. of the original ethylate solution in the presence of methyl orange. The unit of time, t , is the minute. The constants

SODIUM ETHYLATE AND METHYL IODIDE AT 25°.

By H. C. ROBERTSON.

TABLE I.

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide.

A = 10.02.		
t .	α .	Kv.
20	4.34	0.0382
30	5.30	0.0374
42	6.14	0.0376
50	6.52	0.0373
60	6.87	0.0365
<hr/>		
Mean,		0.0374
K_N ,		0.0748

TABLE III.

0.25 N Sodium Ethylate and 0.5 N Methyl Iodide.

A = 10.00.		B = 20.00.
t .	α .	Kv.
10	3.15	0.0207
20	5.08	0.0208
30	6.32	0.0206
40	7.11	0.0200
50	7.70	0.0196
<hr/>		
Mean,		0.0203
K_N ,		0.0812

TABLE II.

0.5 N Sodium Ethylate and 0.25 N Methyl Iodide.

A = 20.00.		B = 10.00.
t .	α .	Kv.
10	2.98	0.0384
20	4.80	0.0380
30	6.01	0.0374
40	6.92	0.0376
50	7.49	0.0365
<hr/>		
Mean,		0.0376
K_N ,		0.0752

TABLE IV.

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide.

A = 10.00.		
t .	α .	Kv.
20	2.93	0.0207
30	3.80	0.0204
40	4.44	0.0200
50	4.98	0.0198
60	5.40	0.0196
<hr/>		
Mean,		0.0201
K_N ,		0.0804

¹ See especially *Am. Chem. J.*, 43, 505 (1910); 49, 116, 127, 369, 474 (1913).

TABLE V.

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
20	1.80	0.0109
30	2.42	0.0107
40	3.00	0.0107
50	3.53	0.0109
70	4.26	0.0106
Mean,		0.0107
K _N ,		0.0856

TABLE VIII.

0.0625 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 20.00.		B = 40.00.
<i>t.</i>	<i>z.</i>	Kv.
20	3.93	0.00577
32	5.79	0.00580
40	6.88	0.00582
60	9.08	0.00579
75	10.33	0.00570
Mean,		0.00577
K _N ,		0.0923

TABLE VI.

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
30	2.43	0.01070
40	3.02	0.01082
50	3.52	0.01086
60	3.90	0.01066
70	4.27	0.01065
80	4.60	0.01064
Mean,		0.01072
K _N ,		0.0858

TABLE IX.

0.025 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 20.00.		B = 100.00.
<i>t.</i>	<i>z.</i>	Kv.
10	2.00	0.00213
20	4.38	0.00250
30	6.60	0.00258
40	7.84	0.00260
50	8.96	0.00250
Mean,		0.00255
K _N ,		0.01020

TABLE VII.

0.0625 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 10.00.		B = 20.00.
<i>t.</i>	<i>z.</i>	Kv.
20	2.00	0.00587
30	2.78	0.00584
40	3.44	0.00580
50	3.99	0.00573
60	4.44	0.00560
Mean,		0.00577
K _N ,		0.0923

TABLE X.

0.025 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide.

A = 20.00.		B = 100.00.
<i>t.</i>	<i>z.</i>	Kv.
20	3.92	0.00223
30	5.84	0.00237
40	7.52	0.00243
50	9.00	0.00248
60	10.28	0.00250
Mean,		0.00244
K _N ,		0.09760

TABLE XI.

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide at 25° C. (1% Water added to the Alcohol used.)

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
20	1.81	0.0110
30	2.50	0.0111
40	3.06	0.0110
50	3.58	0.0111
60	3.96	0.0109
Mean,		0.0110
K _N ,		0.0880

TABLE XIV.

0.5 *N* Sodium Ethylate and 0.5 *N* Methyl Iodide at 25° C. (In a mixture of 90% Alcohol and 10% Ethyl Ether.)

A = 9.98.		
<i>t.</i>	<i>z.</i>	Kv.
30	0.88	0.00322
40	1.153	0.00328
50	1.38	0.00321
60	1.59	0.00316
70	1.81	0.00316
Mean,		0.00320
K _N ,		0.0640

TABLE XII.

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 25° C. (In a soln. contg. 0.92 the mol. equiv. of Sodium Iodide and Ethyl Ether.)

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
20	2.62	0.0178
30	3.46	0.0176
40	4.14	0.0176
60	5.13	0.0175
Mean,		0.0176
K _N ,		0.0704

TABLE XV.

0.5 *N* Sodium Ethylate and 0.5 *N* Methyl Iodide at 25° C. (Flasks coated with a thick layer of black paint so as to be opaque to light.)

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
10	2.77	0.0383
20	4.30	0.0378
30	5.25	0.0368
40	5.90	0.0360
60	6.83	0.0359
Mean,		0.0370
K _N ,		0.0740

TABLE XIII.

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide at 25° C. (In soln. contg. 1.14 the mol. equiv. of Sodium Iodide and Ethyl Ether.)

A = 10.02.		
<i>t.</i>	<i>z.</i>	Kv.
20	1.60	0.0096
40	2.70	0.0092
50	3.18	0.0093
60	3.62	0.0094
Mean,		0.0095
K _N ,		0.0760

TABLE XVI.

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 25° C. (With 0.5 molecular equivalent of Sodium Iodide added.)

A = 10.00.		
<i>t.</i>	<i>z.</i>	Kv.
20	2.64	0.0179
30	3.50	0.0179
40	4.16	0.0178
50	4.74	0.0180
60	5.16	0.0178
Mean,		0.0179
K _N ,		0.0716

TABLE XVII.

0.25 N Sodium Ethylate and 0.25 N
Methyl Iodide at 25° C. (With one
molecular equivalent of Sodium Iodide
added.)

A = 10.00.		
i.	z.	K _v .
25	3.00	0.0171
30	3.38	0.0170
42	4.18	0.0171
70	5.40	0.0168
131	6.91	0.0170

Mean, 0.0170

K_N, 0.0680

TABLE XVIII.

K_N found for Sodium Ethylate and
Methyl Iodide at 25°.

V.	K _N .	K _N average.
2	0.0748	
	0.0752	0.0750
4	0.0812	
	0.0804	0.0808
8	0.0856	
	0.0858	0.0857
16	0.0923	
	0.0923	0.0923
40	0.1020	
	0.0976	0.0998

TABLE XX.

K_i and K_m found for Sodium Ethylate
and Methyl Iodide at 25°.

	K _i .	K _m .
V = 2:V = 4	0.132	0.0577
V = 2:V = 8	0.127*	0.0591*
V = 2:V = 16	0.129*	0.0586*
V = 2:V = 40	0.126*	0.0593*
V = 4:V = 8	0.123	0.0616
V = 4:V = 16	0.127*	0.0595*
V = 4:V = 40	0.125*	0.0605*
V = 8:V = 16	0.130	0.0567
V = 8:V = 40	0.126*	0.0597*
V = 16:V = 40	0.124	0.0632

Average, 0.127 0.0596

Average of values,* 0.127 0.0594

TABLE XIX.

The Ionization of Sodium Ethylate at
25°.

V.	α.	1-α.
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
40	0.605	0.395

TABLE XXI.

K_N calculated and found for Sodium
Ethylate and Methyl Iodide at 25°.

V. K_N found. K_N calculated. Error in %.

K_i = 0.1270. K_i = 0.1270.

K_m = 0.0596. K_m = 0.0594.

2	0.0750	0.0753	0.0752	+0.4	+0.3
4	0.0808	0.0807	0.0805	-0.1	-0.4
8	0.0857	0.0861	0.0860	+0.5	+0.4
16	0.0923	0.0920	0.0919	-0.3	-0.5
40	0.0998	0.1004	0.1002	+0.6	+0.4

Average error, +0.2 +0.4

TABLE XXII.—PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES.

Concentration of NaOC_2H_5 . V.	Per cent of reaction due to αK_i .	Per cent of reaction due to $(1 - \alpha)K_m$.
2	39.5	60.5
4	49.2	50.8
8	58.0	42.0
16	66.5	33.5
40	76.7	23.3

TABLE XXIII.— K_N FOR SODIUM ETHYLATE AND METHYL IODIDE AT 25° , CORRECTED FOR A POSITIVE SALT CATALYSIS OF 8% PER GRAM MOLECULE OF SODIUM ETHYLATE.

V.	α .	$1 - \alpha$.	K_N calculated.	K_N corrected for salt catalysis.
2	0.234	0.766	0.0752	0.0722
4	0.312	0.688	0.0805	0.0789
8	0.393	0.607	0.0860	0.0851
16	0.481	0.519	0.0919	0.0914
40	0.605	0.395	0.1002	0.1000

TABLE XXIV.— K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 25° , CORRECTED FOR POSITIVE SALT CATALYSIS OF 8% PER GRAM MOLECULE OF SODIUM ETHYLATE.

	K_i .	K_m .
V = 2: V = 4	0.1380	0.05210
V = 2: V = 8	0.1343	0.05321
V = 2: V = 16	0.1317	0.05401
V = 2: V = 40	0.1296	0.05467
V = 4: V = 8	0.1538	0.05502
V = 4: V = 16	0.1298	0.05582
V = 4: V = 40	0.1595	0.05646
V = 8: V = 16	0.1285	0.05696
V = 8: V = 40	0.1278	0.05748
V = 16: V = 40	0.1274	0.05804
Average,	0.1360	0.05538

are independent of the laboratory units of concentration employed for the acid; hence K_i , K_m , K_N and K_v refer to the constants for one gram ion of ethylate ions per liter, one gram molecule of nonionized sodium ethylate per liter, etc., as explained in the preceding articles. The addition of considerable quantities of ether and sodium iodide to some of the reaction mixtures shows that the small amounts of these formed during the time periods measured have no great effect on the reaction velocities.

Conclusions.

1. The work presented by Dr. Robertson on the reaction of methyl iodide with sodium ethylate in absolute ethyl alcohol at 25° shows that the reaction is not purely ionic. The "deviation" is strictly proportional to the concentration of the *nonionized* sodium ethylate, and we may,

therefore, interpret the transformation as one involving the reaction of the methyl iodide with both the ethylate ions and the nonionized sodium ethylate.

2. The values $K_i = 0.127$ and $K_m = 0.0596$ agree well with those obtained for methyl iodide and potassium ethylate ($K_i = 0.126$ and $K_m = 0.0687$) by Dr. Julia Peachy Harrison, and for methyl iodide and lithium ethylate ($K_i = 0.1367$ and $K_m = 0.03871$) by Dr. J. H. Shrader. If the theory is correct the true values for K_i should be identical for all three ethylates and the same alkyl halide, and these studies and others, as a whole, confirm this conclusion.

3. The effect of an extra reaction, or "salt catalysis," on these reactions has been calculated.

4. A discussion of the reasons for working with various salts and alkyl halides shows that great care must be exercised in the final interpretation of these results. Chemical reactions are probably far more complex than we can realize with our present limited knowledge.

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ON THE REACTIONS OF BOTH THE IONS AND MOLECULES OF ACIDS, BASES AND SALTS.

A REINTERPRETATION OF THE REACTIONS OF SODIUM METHYLATE AND SODIUM ETHYLATE WITH 1,2-DINITROBENZENE, 1,2,4-DINITROCHLOROGENE AND 1,2,4-DINITROBROMOBENZENE.¹

[TWENTY-SECOND² COMMUNICATION ON CATALYSIS.]

By S. F. ACRER.

Received April 15, 1915.

The very fine work of Hecht,³ Conrad and Brückner on the action of sodium ethylate on alkyl halides, and that of Bruyn, Steger,⁴ and Lulofs⁵ on the reactions of sodium methylate and sodium ethylate with the nitro and halogen substitution products of benzene were not interpreted by them by the use of the ionization theory. Conrad⁶ and his co-workers spoke of these substances as nonelectrolytes, or "nichtleitende Körper." Bruyn and his co-workers, while measuring the conductivities of the sodium methylate and sodium ethylate, recognized that they were dealing with peculiar cases that could not be explained on the ionization hypothesis alone. In a footnote⁷ Bruyn suggested that his reactions may

¹ We are indebted to the Carnegie Institution of Washington for aid in this work.

² See especially *Am. Chem. J.*, 48, 352 (1912); 49, 116, 127, 345, 369, 474 (1913).

³ *Z. physik. Chem.*, 5, 289 (1890). A similar reinterpretation of this excellent work will soon be published by Dr. W. A. Taylor.

⁴ *Ibid.*, 49, 329; 333, 336 (1904); *Rec. trav. chim.*, 18, 13, 41.

⁵ *Z. physik. Chem.*, 49, 341 (1904); *Rec. trav. chim.*, 20, 292.

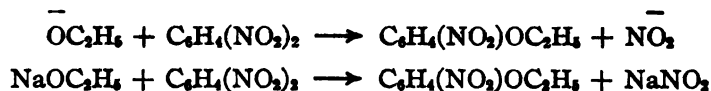
⁶ *Z. physik. Chem.*, 5, 289 (1890).

⁷ *Rec. trav. chim.*, 18, 40; see also *Z. physik. Chem.*, 49, 332 (1904).

be different from those of Hecht, Conrad and Brückner and that, perhaps, "l'alcoholate s'unit d'abord au groupe AzO_2 par addition aet qu'a cette addition les molecules non dissociees prennent part exclusivement." They apparently overlooked the fact, however, that such a hypothesis must lead to a decrease¹ in the reaction velocity, K_N , as the concentration of the methylate or ethylate decreases and the percentage of non-ionized electrolyte decreases. As their reaction velocities never decreased, but remained constant or increased, their suggestion hardly meets the requirements of the mass law and the theory of ionization.

An inspection of the data in all these cases shows that *the reaction velocity is larger than that calculated on the hypothesis that the ethylate or methylate ions alone are active*. It was just such cases as these, and others, that lead the writer to see that this "deviation from the ionic reaction" could be due to the molecular sodium methylate or ethylate instead of to a so-called "salt catalysis," and to begin with Brunel in 1905, work on the theory that both the ions and nonionized forms of acids, bases and salts are chemically active.

The reactions discussed in this paper can be readily interpreted as transformations of both the anions and molecules of sodium ethylate and sodium methylate, as follows:



The equation $K_N = K_i\alpha + K_m(1 - \alpha)$, developed in earlier papers,² gives excellent constants for K_i and K_m in Table II of each section. The reaction velocities " K_N found" in Table I of each section are those recorded by Bruyn, Steger³ and Lulofs. The ionization α , in Table I of each section, of the sodium ethylate is obtained from our own data,⁴ while the ionization of the sodium methylate is obtained from Table V of S. Tijmstra Bz⁵ by extrapolating to $M_\infty = 85$ in absolute methyl alcohol and $\mu_\infty = 80$ in 90.3% methyl alcohol. Since the values of K_m are very large in all cases, any small error in the ionizations resulting from this extrapolation will not invalidate the conclusion that the non-ionized methylate or ethylate is active. As the following table shows, the values of K_m are from 25% to 100% of those of K_i .

By substituting these values for K_i and K_m , and the proper ones for α in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$, it is shown in Table I of each section in the experimental portion that the " K_N calculated" agrees

¹ *Am. Chem. J.*, 38, 273 (1907); 39, 226-231 (1908), and all the later papers.

² *Ibid.*, 39, 226 (1908); 43, 519 (1910) and later articles.

³ *Z. physik. Chem.*, 49, 331, 341, 342 (1904).

⁴ *J. Phys. Chem.*, 19, 381 (1915).

⁵ *Ibid.*, 49, 349 (1904).

	K_i	K_m	K_i/K_m
Sodium ethylate and <i>o</i> -dinitrobenzene in absolute ethyl alcohol at 45°.....	0.229	0.230	1.0
Sodium methylate and <i>o</i> -dinitrobenzene in absolute methyl alcohol at 45°.....	0.1458	0.1278	1.2
Sodium methylate and 1,2,4-dinitrochlorobenzene in 90.3% methyl alcohol at 15°.....	1.376	0.759	1.8
Sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute methyl alcohol at 15°.....	1.299	0.724	1.8
Sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute ethyl alcohol at 15°.....	2.838	0.823	3.4
Sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute alcohol at 15°.....	4.473	1.195	3.8

excellently with the K_N found experimentally by Bruyn, Steger and Lulofs, the "Error in percentage" in Table I of each section being generally small. The "percentage of reaction due to ions and to molecules" is given in Table III of each section.

Since the ethylate ion and the sodium ethylate molecules react with the same velocities with the *o*-dinitrobenzene, the change of the ethylate ions into the sodium ethylate molecules by the addition of sodium nitrite and sodium acetate should have no effect on the reaction velocity: this requirement of the theory is substantiated by the experiments,¹ and there is no noticeable "abnormal salt catalysis." Likewise the addition of sodium iodide to sodium ethylate and 1,2,4-dinitrochlorobenzene lowers the reaction velocity, in conformity with the theory, because the more active ethylate ions are partially converted into the less active sodium ethylate molecules.²

The writer is greatly indebted to Dr. W. A. Taylor and Mr. E. C. White for making the calculations.

Experimental.

On the reactions of sodium ethylate and *o*-dinitrobenzene at 45°.

TABLE I.—THE IONIZATIONS, K_N CALCULATED AND FOUND, AND PERCENTAGE ERROR FOR SODIUM ETHYLATE AND *o*-DINITROBENZENE AT 45°.

V.	α .	1 — α .	K_N found. ³	K_N calculated.	Error in per cent.
20	0.465	0.535	0.230	0.229	+0.4
40	0.563	0.437	0.229	0.229	0.0
60	0.631	0.369	0.229	0.229	0.0
80	0.670	0.330	0.230	0.229	+0.4
100	0.704	0.296	0.229	0.229	0.0

¹ *Z. physik. Chem.*, 49, 332 (1904).

² *Ibid.*, 49, 342 (1904).

³ In this article we have used the values of K_N given, without attempting to verify them by recalculations or experiments.

TABLE II.— K_i AND K_m FOUND FOR SODIUM ETHYLATE AND *o*-DINITROBENZENE AT 45°.

	K_i	K_m
V = 20:V = 40	0.2245	0.2347
V = 20:V = 60	0.2270	0.2338
V = 20:V = 80	0.2300	0.2300
V = 20:V = 100	0.2277	0.2320
V = 40:V = 60	0.2290	0.2290
V = 40:V = 80	0.2290	0.2237
V = 40:V = 100	0.2321	0.2290
V = 60:V = 80	0.2385	0.2130
V = 60:V = 100	0.2290	0.2290
V = 80:V = 100	0.2203	0.2490
Average,	0.2287	0.2302

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i	Percentage of reaction due to $(1 - \alpha) K_m$
20	46.4	53.6
40	56.2	43.8
60	63.0	37.0
80	66.9	33.1
100	70.3	29.7

On the reactions of sodium methylate and *o*-dinitrobenzene at 45°.

TABLE I.—THE IONIZATIONS, K_N CALCULATED AND FOUND, AND THE ERROR IN PER CENT. FOR SODIUM METHYLATE AND *o*-DINITROBENZENE AT 45°.

V.	α	$1 - \alpha$	K_N found.	K_N calculated.	Error in per cent.
20	0.596	0.404	0.1385	0.1385	0.0
40	0.671	0.329	0.1400	0.1398	+0.1
80	0.734	0.266	0.1410	0.1410	0.0

TABLE II.— K_i AND K_m FOR SODIUM METHYLATE AND *o*-DINITROBENZENE AT 45°.

	K_i	K_m
V = 20:V = 40	0.1465	0.1265
V = 20:V = 80	0.1458	0.1277
V = 40:V = 80	0.1452	0.1293
Average,	0.1458	0.1278

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i	Percentage of reaction due to $(1 - \alpha) K_m$
20	62.7	37.3
40	69.9	30.1
80	76.5	23.5

On the reactions of sodium methylate and 1,2,4-dinitrochlorobenzene in 90.3 per cent. methyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND THE ERROR IN PER CENT. FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α	$1 - \alpha$	K_N found.	K_N calculated.	Error in per cent.
20	0.696	0.304	1.20	1.187	+1.09
33.33	0.742	0.258	1.21	1.216	-0.49
100	0.815	0.185	1.28	1.261	+1.50

TABLE II.— K_i AND K_m FOUND FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

		K_i	K_m
V = 20	:V = 33.33	1.266	1.048
V = 20	:V = 100	1.404	0.732
V = 33.33	:V = 100	1.457	0.498
Average,		1.376	0.759

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i	Percentage of reaction due to $(1-\alpha) K_m$
20	80.6	19.4
33.33	83.9	16.1
100	88.8	11.2

On the reactions of sodium methylate and 1,2,4-dinitrochlorobenzene in absolute methyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND ERROR IN PER CENT. FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α	$1-\alpha$	K_N found.	K_N calculated.	Error in per cent.
20	0.661	0.339	1.10	1.104	-0.36
33.33	0.717	0.283	1.14	1.136	+0.35
100	0.805	0.195	1.18	1.186	-0.50

TABLE II.— K_i AND K_m FOUND FOR SODIUM METHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

		K_i	K_m
V = 20	:V = 33.33	1.342	0.627
V = 20	:V = 100	1.288	0.732
V = 33.33	:V = 100	1.268	0.814
Average,		1.299	0.724

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i	Percentage of reaction due to $(1-\alpha) K_m$
20	77.7	22.3
33.33	81.9	18.1
100	88.1	11.9

On the reactions of sodium ethylate and 1,2,4-dinitrobromobenzene in absolute alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND AND ERROR IN PER CENT. FOR SODIUM ETHYLATE AND 1,2,4-DINITROBROMOBENZENE AT 15°.

V.	α	$1-\alpha$	K_N found.	K_N calculated.	Error in per cent.
20	0.525	0.475	1.88	1.880	0.00
33.33	0.603	0.397	2.04	2.038	+0.09
100	0.749	0.251	2.33	2.332	-0.08

TABLE II.— K_i AND K_m FOUND FOR SODIUM ETHYLATE AND 1,2,4-DINITROBROMOBENZENE AT 15°.

		K_i	K_m
V = 20	:V = 33.33	2.854	0.803
V = 20	:V = 100	2.834	0.825
V = 33.33	:V = 100	2.828	0.842
Average,		2.838	0.823

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i	Percentage of reaction due to $(1-\alpha) K_m$
20	79.2	20.8
33.33	83.9	16.1
100	91.1	8.9

On the reactions of sodium ethylate and 1,2,4-dinitrochlorobenzene in absolute ethyl alcohol at 15°.

TABLE I.—THE IONIZATION, K_N CALCULATED AND FOUND, AND ERROR IN PER CENT. FOR SODIUM ETHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	α .	1 — α .	K_N found.	K_N calculated.	Error in per cent.
20	0.5258	0.4742	2.94	2.92	+0.75
33.33	0.6037	0.3963	3.26	3.17	+2.74
100	0.7497	0.2503	3.56	3.65	—2.51

TABLE II.— K_i AND K_m FOUND FOR SODIUM ETHYLATE AND 1,2,4-DINITROCHLOROBENZENE AT 15°.

V.	K_i .	K_m .
V = 20 : V = 33.33	4.887	0.814
V = 20 : V = 100	4.253	1.484
V = 33.33 : V = 100	4.279	2.019
Average,	4.473	1.195

TABLE III.—PERCENTAGE OF REACTION DUE TO IONS AND TO MOLECULES.

V.	Percentage of reaction due to αK_i .	Percentage of reaction due to $(1 - \alpha)K_m$.
20	80.59	19.41
33.33	85.08	14.92
100	91.80	8.20

Conclusions.

The work of Bruyn, Steger and Lulofs on the reactions of sodium methylate and sodium ethylate on 1,2-dinitrobenzene, 1,2,4-dinitrochlorobenzene and 1,2,4-dinitrochlorobenzene can be reinterpreted excellently as transformations of both the ethylate and methylate ions and the non-ionized sodium ethylate and sodium methylate.

The value of K_m , the activity of the nonionized electrolyte per gram molecule per liter, is from 25% to 100% as large as the value of K_i , the activity of the methylate or ethylate ion per gram ion per liter.

These results harmonize excellently with (a) about 30 reactions which we have investigated experimentally, with (b) a large number of our re-interpretations of the work of others, and with (c) the results obtained recently by Arrhenius,¹ Goldschmidt,² Bredig,³ Stieglitz,⁴ Dawson,⁵ Kilpi,⁶ Holmberg,⁷ Biddle⁸ and Worley.⁹

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¹ Taylor and Arrhenius, *Memoirs of the Nobel Institute*, 2, Nos. 34, 35, 37.

² *Z. Elektrochem.*, 15, 6; *Z. physik. Chem.*, 70, 627 (1910).

³ *Z. Elektrochem.*, 18, 535, 543; *Z. physik. Chem.*, 85, 129, 170, 211 (1913).

⁴ THIS JOURNAL, 34, 1687, 1688, 1689, 1690, 1694 (1912); 35, 1774 (1913).

⁵ *J. Chem. Soc.*, 103, 2135 (1913).

⁶ *Z. physik. Chem.*, 86, 427, 644, 740 (1914).

⁷ *Ibid.*, 84, 451, 468, 469 (1913).

⁸ THIS JOURNAL, 36, 99 (1914), and earlier papers.

⁹ *Phil. Mag.*, 27, 459.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

A STUDY OF THE REACTIONS OF SODIUM MALONIC ESTER.¹

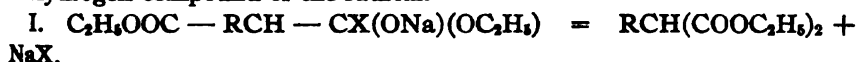
[SECOND PAPER.]

BY C. LORING JACKSON AND F. C. WHITMORE.

Received June 17, 1915.

In a previous paper² we have given experimental proofs of the existence of one of the addition compounds predicted by the theory of malonic ester reactions proposed by H. E. Bigelow and one of us³ (but earlier by Von Findeisen⁴). In this paper we take up the remainder of our theory, and show that the course of the reaction depends in great measure on the relative attractions of the two parts of the substance added for the carbon attached to the sodium.

The theory may be briefly stated as follows: When an organic substance containing a halogen reacts with sodium malonic ester, the first stage is the addition of one atom of the halogen and the residual organic radical to the (enol) sodium malonic ester. If the halogen (X) has a greater attraction for the carbon carrying the sodium than the organic radical (R) has, it will be attached to it (I); and this will break up into sodium halide and substituted malonic ester. If, however, the organic radical (R) happens to have the stronger attraction for the carbon attached to the sodium, it will combine with this, giving the addition compound II, which will decompose into halogen malonic ester and either the sodium or hydrogen compound of the radical.



The object of this paper is to study the conditions which cause the replacement of halogen by hydrogen (or sodium), under the influence of sodium malonic ester (II). According to our theory this takes place when the organic radical is more attracted than the halogen by the carbon carrying the NaO. In discussing Nef's theory of the hydrogen replacement⁵ in our first paper, we brought forward as a grave objection to it the fact that it required the sodium to prefer the negative organic radical to the halogen. This objection does not apply to our theory, as according to it sodium itself does not attract the halogen or the organic radical, but an atom of carbon rendered positive by NaO, and in view of the fact

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Frank Clifford Whitmore.

² THIS JOURNAL, 37, 1522 (1915).

³ *Am. Chem. J.*, 46, 549 (1911).

⁴ *J. prakt. Chem.*, 65, 530 (1902).

⁵ *Ann.*, 308, 306 (1899); *Am. Chem. J.*, 32, 449 (1904).

that the attraction of carbon for halogen is not very strong at best, it seems not an unjustifiable supposition that this might prefer a strongly negative carbon atom to the halogen. Such a hypothesis, however, can be accepted only when supported by a large mass of evidence, and therefore in this paper we show that all the experimental results we have been able to find, are satisfactorily explained by our theory with a single exception—bromide of cyanogen—in which case sufficient data for a complete discussion are wanting.

The following list contains, we think, all the well-established cases, in which the halogen of an organic compound is replaced by hydrogen or sodium under the influence of a sodium ester.

Work in this laboratory has led to the discovery of the following cases, in which a halogen was replaced by hydrogen in nitrohalogen aromatic compounds. In this list the constitution of the substance is indicated by its formula, and the halogen replaced is printed in *italics*. The other reagent was sodium malonic ester, except where noted. $C_6NO_2BrHBrNO_2Br$,¹ also with sodium acetoacetic ester,² $C_6NO_2BrNO_2BrNO_2Br$,³ $C_6NO_2BrBrBrNO_2Br$,⁴ $C_6NO_2IHINO_2I$,⁵ $C_6NO_2IBrINO_2I$ ⁶ and perhaps $C_6HBrOHBrOHBr$,⁷ although only the ethanetetra-carboxylic ester could be detected in this case.

When, in beginning this study of our theory, we searched for halogen compounds with organic radicals negative enough to give the hydrogen replacement, the most promising seemed to be phenylsulfochloride, which, according to our theory, should give with sodium malonic ester, sodium phenylsulfinate and chloromalonic ester (or ethanetetra-carboxylic ester). Upon looking up the literature, however, we found that this experiment had been tried already by Kohler and MacDonald⁸ with *p*-tolylsulfochloride, and had given exactly the results predicted by us. Sodium acetoacetic ester also behaved in the same way (repeated later by von Findeisen⁹), and so did phenylsulfochloride and sodium camphocarboxylic ester as observed by Brühl.¹⁰ We have also tried the action of phenylsulfochloride on sodium malonic ester with the formation of the sulfinate and ethanetetra-carboxylic ester.

Closely related to these observations is the formation of sodium ethyl-

¹ Jackson, Robinson, *Am. Chem. J.*, **11**, 93, 448 (1889).

² Jackson, Moore, *Ibid.*, **12**, 164, (1890).

³ *Ibid.*, **7**, (1890).

⁴ Jackson, Bancroft, *Ibid.*, 289 (1890).

⁵ Jackson, Langmaid, *Ibid.*, **32**, 297 (1904).

⁶ Jackson, Bigelow, *Ibid.*, **46**, 549 (1911).

⁷ Jackson, Dunlap, *Ibid.*, **18**, 111 (1896).

⁸ *Ibid.*, **22**, 232 (1899).

⁹ *J. prakt. Chem.*, **65**, 530 (1902).

¹⁰ *Ber.*, **35**, 4113 (1902).

sulfite and ethanetetra-carboxylic ester from ethylsulfuric chloride, $C_2H_5-OSO_2Cl$, observed by Willcox,¹ when sodium malonic ester was the other reagent. Sodium acetoacetic ester also gave the sulfite. Less closely related is Bischoff's² conversion of diethyldisulfonemethanediiodide, $(C_2H_5SO_2)_2CI_2$, into diethyldisulfonemethane with ethylenetetra-carboxylic ester as the secondary product. The formation of the ethylene, instead of the ethane compound, is probably due to a secondary reaction. In all the cases so far mentioned the organic radical is strongly negative. In Kohler's³ ethyl- and ethylenesulfocyanates, which gave with sodium acetoacetic ester disulfides (through the mercaptids), the organic radicals are less negative, but as in this case they are opposed to such a very weak negative radical as cyanogen, they might well take the position next the sodium. Kohler's interesting observation that the copper acetoacetic ester gave better results than the sodium salt may be caused by the fact that copper has a stronger attraction for sulfur than sodium has, as well as by the insolubility of the copper mercaptid. In continuation of this line of work we tried the action of 1-bromomercapto-2,4-dinitrobenzene, $C_6H_3(NO_2)_2SBr$, with sodium malonic ester, and obtained a little mercaptan and much disulfide, part of which may have been formed from mercaptan. In this case the attraction of the sulfur and phenyl for the positive carbon is reinforced by the two nitro groups, and thus may be made greater than that of the bromine.

Nef⁴ has found that the 1²-bromo- or iodophenylacetylene gave phenylacetylene and ethanetetra-carboxylic ester with sodium malonic ester, and that sodium acetoacetic ester acted in the same way, while the chloro compound $C_6H_5C \equiv Cl$ gave a product derived from the union of the phenylacetylene radical with malonic ester. The well-known formation from acetylene of metallic derivatives (copper or sodium) indicates a strong attraction for positive radicals, which in this case, reinforced by phenyl, might well overcome the attraction of the bromine or iodine for the positive carbon, but not the stronger one of the chlorine.

In our own work on this subject we felt an especial interest in benzoyl-iodide, which, according to our theory, might give, with sodium malonic ester, benzaldehyd in addition to the benzoylmalonic ester—the sole organic product of the action with the chloride or bromide; and, in fact, our experiments yielded a substance showing many of the properties of benzaldehyd, but differing from it in such an important particular that its formation cannot be considered established without much more work, which unfortunately we were unable to give to it. This work, there-

¹ *Am. Chem. J.*, 32, 474 (1904).

² *Ber.*, 30, 488 (1897).

³ *Am. Chem. J.*, 22, 68 (1899).

⁴ *Ann.*, 308, 305, 316, 321 (1899).

fore, is not used in the discussion of our theory. On the other hand, as we expected, nitrobenzoylchloride gave no aldehyd.

We have found also that bromomethanetricarboxylic ester, $\text{BrC}(\text{COOC}_2\text{H}_5)_3$, is converted into methanetricarboxylic ester by sodium malonic ester, and that α -bromodiphenylpropionophenone has the atom of bromine replaced by hydrogen.

While we were writing this paper we received an account of similar replacements of bromine by hydrogen in bromylphthalimide and bromylsuccinimide observed by Scheiber and Haun.¹ The reagents used were sodium malonic ester, or sodium cyanoacetic ester, and the same result was probably obtained with sodium acetoacetic ester, although in this case only the diacetosuccinic ester was detected.

The classes of compounds enumerated above have furnished 29 cases of the replacement of halogen by hydrogen (or sodium); and we can find only one thing which they have in common—all contain strongly negative radicals. Further, this negativity is produced in a great variety of ways: by nitrohalogenphenyl, oxygen compounds of sulfur, sulfur alone (in the sulfo cyanates), or reinforced by nitrophenyl, phenylacetylene, carboxyl-ester groups, phenylketones or imides of dibasic acids. This seems to us a very strong argument for our theory.

There remain to be considered only 10 cases of the replacement of halogen by hydrogen, in all of which the radical combined with the halogen is negative, but perhaps not enough so to be preferred to the halogen by the positive carbon. They belong in three classes: Reactions of substituted alkylmalonic esters, of polyhalides, and of bromide of cyanogen, and each will be discussed in detail.

Ruhemann² found that bromomethylmalonic ester and sodium malonic ester gave methylmalonic ester and ethylenetetracarboxylic ester,³ and that the ethyl compound behaved in the same way. These results were confirmed by Bischoff,⁴ who also extended them to the chloroesters, and added similar results from the action of chloro- or bromomalonic esters on sodium methyl- or ethylmalonic esters. Later in this introduction will be found a discussion of the radicals giving the hydrogen replacement, from which it appears that the malonic ester and alkylmalonic ester radicals are among the least negative that produce it. Taking Ruhemann's reaction of bromomethylmalonic ester as an example the theory would predict, therefore, that both the addition compounds III and IV would be formed, some molecules giving one, some the other, so that we should

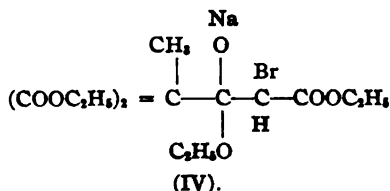
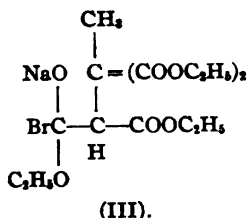
¹ *Ber.*, 47, 3335 (1914).

² *Ibid.*, 26, 2357 (1893).

³ We have shown that the formation of the ethylene ester is due to the use of heat. In the cold ethanetetracarboxylic ester is formed.

⁴ *Ber.*, 29, 1511 (1896).

expect a considerable yield of the substituted malonic ester formed from III,¹ and its comparative absence in the actual experiments needs explanation.



tion. The amounts formed of the two addition compounds (III) and (IV) will depend, in part, on the relative negativity of the halogen and organic radical, in part on the other conditions, and in every case will tend to reach an equilibrium; but they are so unstable that this equilibrium will be established between the products of their decomposition rather than between the addition compounds themselves. The decomposition of (IV) is represented by the following reaction:



that is, it falls into sodium methylmalonic ester and bromomalonic ester, but the latter will react at once with the excess of sodium malonic ester, since this reaction has been found to take place essentially instantaneously, whereas reactions involving alkylmalonic esters (whether bromo or sodium) are very sluggish. As soon, therefore, as the reaction has taken place, the bromomalonic ester will be converted into ethanetetra-carboxylic ester, and the equilibrium being broken in this way, more of (IV) will be formed again and again in the effort to restore it, thus producing the large yield of ethanetetra-carboxylic ester, while the substituted malonic ester produced from (III) will be reduced to a very small amount; and, as a matter of fact, Bischoff found that in all these experiments such minute quantities of the substituted malonic esters were obtained.

The other case where bromomalonic ester acts with sodium methylmalonic ester can be explained in the same way, but it is not necessary to give the details. On the other hand, we should explain why bromomalonic ester and sodium malonic ester give only the substituted malonic ester (in this case the ethanetetra-carboxylic ester), whereas, since $-\text{CH}(\text{COOC}_2\text{H}_5)_2$ is more negative than $-\text{CCH}_2(\text{COOC}_2\text{H}_5)_2$, a greater amount of hydrogen replacement would be predicted. This is due to the fact that the addition product corresponding to (IV) can decompose only into the original reagents (bromomalonic ester and sodium malonic ester), so that

¹ This would be especially the case with the chloro compounds.

here new products can be formed only by the addition corresponding to (III).

Two cases of replacement of halogen by hydrogen have been observed with polyhalides. Tetrachloride of carbon¹ gives with sodium malonic ester a derivative of chloroform and ethanetetracarboxylic ester; and tetraiodoethylene² gives acetylene and ethanetetracarboxylic ester. To explain the action of tetrachloride of carbon our theory requires that the radical CCl_3 — should be more strongly attracted by the carbon carrying the sodium than free chlorine, which is certainly hard to believe; and yet the following considerations (if they are not too fanciful), justify this idea. The strong attraction for sodium residing in each atom of chlorine will be only partially neutralized by the union of the chlorine with carbon, for which it has much less attraction. It may be possible, therefore, that the residual attractions of the 3 atoms of chlorine left after union with the one atom of carbon should together exercise a stronger attraction for the positive carbon than the entire attraction of the single atom of free chlorine. This explanation would apply even better to the case of tetraiodoethylene, as it contains the less negative iodine.

Chloride of cyanogen gives cyanomalonic ester.³ The bromide gives hydrocyanic acid and ethanetetracarboxylic ester.⁴ At first sight this seems to be in accord with our theory as bromine should be replaced by hydrogen, when chlorine is not, but a more careful consideration shows this is not the case, because bromine is certainly more negative than cyanogen, and therefore the bromide should yield cyanomalonic ester instead of hydrocyanic acid. This is the only observation we have found, which is out of harmony with our theory. It may be caused by the intervention of other conditions, such as differences in solubility of the products, or of constitution in the cyanogen compounds, but at present not enough facts are known to decide whether this is the case. It is also possible that the effect of such other conditions may explain the reaction of tetrachloride of carbon rather than the theory proposed above.

We have considered now all the undoubted cases of hydrogen replacement, and have found only 1, bromide of cyanogen, which does not support our theory. In all these cases the hydrogen replacement was proved by the identification of its direct products. There are a few others, in which it can be inferred as an intermediate stage to interpret the actual results,⁵ but in all these there may be other possible interpretations and so we prefer to omit them from our discussion, although they tell in our

¹ Dimroth, *Ber.*, 35, 2881 (1902).

² Bischoff, *Ibid.*, 28, 2832 (1895).

³ Haller, *Ann. chim. phys.*, [6] 16, 419 (1889).

⁴ Nef, *Ann.*, 298, 260 note (1897).

⁵ Büchner, *Ibid.*, 284, 223; Knoevenagel, *Ber.*, 21, 1355.

favor. We also leave out cases in which a ring is formed,¹ as this always introduces a disturbing condition, which may even prove to be the controlling one.

The foregoing discussion furnishes a strong argument in favor of our theory, as in every case of hydrogen replacement a distinctly negative organic radical takes part as was predicted, and it is further strengthened by considering the substances, which give the other—the malonic—replacement, as they on the whole are less negative. Thus the most negative substances which give this malonic replacement exclusively, are the acyl halides (except perhaps benzoyliodide), iodoanil, and benzal bromoacetophenone, to which should be added $\text{BrC}(\text{COOC}_2\text{H}_5)_2\text{CH}_2\text{COOC}_2\text{H}_5$ and $\text{BrCCOOC}_2\text{H}_5(\text{CH}_2\text{COOC}_2\text{H}_5)_2$, if these react normally, but there is good reason to think that in these cases the reaction consists in the removal of hydrobromic acid, followed by addition of malonic ester.

As, however, we have no strict method for the quantitative determination of negativity, so that it is in large measure a matter of judgment, a general comparison is less satisfactory than one confined to series of related substances, in which the negativity is produced by the same radical. The best case of this sort we have found is given in the following table:

$\text{BrC}(\text{COOC}_2\text{H}_5)_2$	Replacement by hydrogen only.
$\text{BrCH}(\text{COOC}_2\text{H}_5)_2$	Replacement by hydrogen with a little malonic ester. ²
$\text{BrCH}_2(\text{COOC}_2\text{H}_5)_2$	Replacement by malonic ester only.

Here the nature of the reaction changes as the negativity of the radical decreases, exactly as predicted by our theory. Another similar case is the formation of a malonic ester derivative from chloroform, while in tetrachloride of carbon the fourth chlorine is replaced by hydrogen.

According to our theory the replacement of halogen by hydrogen is to be expected with bromine, iodine, or cyanogen, but only in exceptional cases with chlorine. As a matter of fact, of the 39 cases of this reaction known only 10 take place with chlorine compounds, and 5 of these are the exceptional cases anticipated, in which the radicals (containing sulfur and oxygen) associated with the chlorine are so negative that they may well be more strongly attracted by the positive carbon. The remaining 5, however—4 cases of chloromalonic esters and tetrachloride of carbon—are not directly in harmony with our theory, as their organic radicals belong to the least negative, with which such reactions have been observed. Our attempts to explain away these objections have been given already. A marked confirmation of the theory is found in Kohler's³ work on the ethyl- and ethylenesulfocyanates, where but slightly negative radicals

¹ For instance, Gutzeit, Engelmann, *J. prakt. chem.*, 66, 123 (1902); Perkin, *J. Chem. Soc.*, 59, 822 (1891).

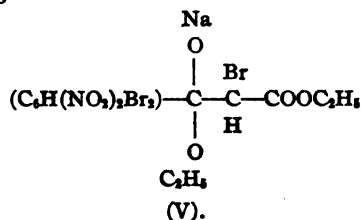
² When reacting with sodium methylmalonic ester.

³ *Am. Chem. J.*, 22, 68 (1899).

brought about the replacement by hydrogen, and this should be the case, when the halogen is cyanogen, the most feebly negative member of the group.

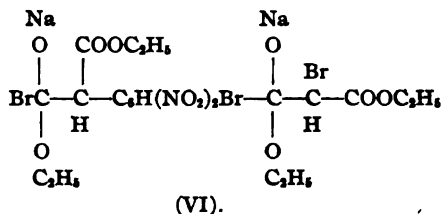
We would also call attention to the fact that our theory explains both the hydrogen replacement reactions and those in which substituted malonic esters are formed, whereas Nef used different theories¹ to explain these two sets of reactions.

Another strong point in favor of our theory is that it explains many complex chemical processes, which without it were decidedly obscure. For instance, 1,3,5-tribromo-2,4-dinitrobenzene with sodium malonic ester gives bromodinitrophenylmalonic ester,² the formation of which can be explained as follows: The first step would be the formation of the addition compound (V) because of the strongly negative character of the nitrobenzene organic radical.



That this is the first stage of such reactions has been proved by the work of H. E. Bigelow and one of us on triiodobromodinitrobenzene.³

The addition compound (V) still contains a reactive atom of bromine, and therefore adds to a second molecule of sodium malonic ester, breaking for this purpose into bromine and $[\text{C}_6\text{HBr}(\text{NO}_2)_2\text{C}(\text{ONaOC}_2\text{H}_5)\text{CHBrCOOC}_2\text{H}_5]$, but, as this complex radical contains an atom of sodium, its negativity will be so reduced that it will not be preferred to the bromine by the positive carbon, so the new addition compound will have the formula (VI).



This, on acidification, will yield sodium bromide, bromodinitrophenylmalonic ester, and bromomalonic ester (which could give ethanetetra-carboxylic ester), the actual products of the reaction.

¹ *Ann.*, 298, 263 (1897); *Ibid.*, 308, 306 (1899).

² Jackson, Robinson, *Am. Chem. J.*, 11, 93 (1889).

³ *Ibid.*, 46, 549 (1911).

The fact that the third atom of bromine cannot be replaced either by hydrogen, or the malonic ester radical, is also explained by our theory. As is well known, bromine can be removed from the benzene ring only, when this is strongly negative, and in a compound like (VI) we should expect the two atoms of sodium to diminish the loosening effect of the two nitro groups, or even to destroy it, as was found to be the result here. If, however, there were three nitro groups present instead of two, we should not expect the reactivity of the last bromine to be completely destroyed by the two atoms of sodium, although it should be much diminished, and, as a fact, tribromotrinitrobenzene forms in the cold bromotrinitrophenylmalonic ester, in which the last bromine is retained; but if boiled with sodium malonic ester, this bromine also enters into reaction, and trinitrophenylenedimalonic ester is formed.

The explanation given above will not apply without modification to the behavior of triiodobromodinitrobenzene¹ which gives in the cold diiodobromodinitrobenzene, but this product, when heated with sodium malonic ester, forms iodobromodinitrophenylmalonic ester. Here the negativity of the organic radical cannot be reduced as in the preceding case, so a different way of converting the diiodobromodinitrobenzene into a sodium compound must be sought; and this is supplied by some work by Gazzolo and one of us,² which showed that sodium malonic ester combines with trinitrobenzene to form $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$. The conformation necessary for such an addition was proved to be a nitro group in the ortho position to an atom of hydrogen or some other indifferent radical and, as in the diiodobromodinitrobenzene we have one such conformation, it seems certain that it will take up one molecule of sodium malonic ester, thus producing the reduction of its negativity required by our theory.

The formation of ethanetetra-carboxylic ester in place of halogen malonic ester in many of our experiments needs some explanation, because the halogen malonic ester is not formed until the addition compound is destroyed by acidification, and it would seem this must destroy the sodium malonic ester necessary to form the tetracarboxylic ester; but, as a fact, in such cases the acidification took place by shaking the benzene solution with an aqueous acid, and was such a slow process that part of the sodium and halogen malonic esters had time to react on each other, before the whole of the former was destroyed.

An objection to our theory might be found in the speed with which the addition compounds leading to the hydrogen replacement are decomposed, since this action consists of the breaking apart of two atoms of carbon, which generally takes place less easily; but it is to be observed that both the

¹ Jackson, Bigelow, *Am. Chem. J.*, 46, 549 (1911).

² *Ibid.*, 23, 388 (1900).

organic radicals are highly negative; and under these circumstances decomposition is often easy, as, for instance, in the decomposition of chloral by an alkali, and of hexabromodiacetyl, which is split by very weak alkaline reagents into bromoform and oxalic acid, while even water at 100° forms bromoform with it, according to observations made in this laboratory. The fact that one product of the decomposition is the very stable carboxethyl in our case would also make it take place more easily.

It might also be objected to our theory that it does not explain the reactions of sodium alcoholates with halogen nitro aromatic compounds, which give in some cases alkyl ethers, in others replacement of halogen by hydrogen, and therefore seem to be parallel to the reactions with sodium malonic ester. The absence of a double bond in these reagents makes it impossible to bring the cases directly under our theory, and we have found no modification of it that we feel able to accept, the formation of addition compounds containing quadrivalent oxygen, for instance, being contrary to all known analogy. If, then, the sodium alcoholate reactions are parallel to those with sodium malonic ester, they certainly involve an objection to our theory; but this relation between them is more apparent than real, as can be shown by a few differences. The phenylsulfochloride, if the reaction is parallel to that with sodium malonic ester, should give with sodium ethylate sodium sulfinic ester, whereas instead the product is phenylsulfonic ester. Tribromotrinitrobenzene also gives, with sodium malonic ester, bromotrinitrophenylmalonic ester, but with sodium ethylate a mixture of trinitrophenylglucineethyl ether and of tribromonitroresorcinethyl ether. It seems to us that these and similar differences justify the explanation of these sets of reactions by different theories, and therefore remove this possible objection to our theory, of the sodium malonic reactions.

Summary of the Evidence in Regard to the Theory.

1. One of the addition compounds predicted by it has been prepared in a pure state, and analyzed, as described in the first paper.
2. All the compounds, which give with sodium malonic ester the replacement of halogen by hydrogen, contain strongly negative radicals; those forming substituted malonic esters contain less negative radicals.
3. The replacement by hydrogen generally occurs with the less negative halogens—bromine, iodine or cyanogen. In the few cases in which chlorine is replaced by hydrogen, either it is associated with an exceptionally negative radical, or the action can be explained more or less satisfactorily by the intervention of other conditions.
4. The theory offers a satisfactory explanation of both classes of reactions.
5. It explains clearly complex organic processes, which without it were very obscure.

6. A possible objection that breaking apart two carbon atoms would not take place so easily as the decomposition of the addition compound leading to the hydrogen replacement was met by comparison with chloral and hexabromodiacyetyl.

7. An objection that it does not explain the parallel reactions with sodium alcoholates was met by citing experiments to show that the two classes of reactions are really not parallel.

Experimental.

Action of Phenylsulfochloride on Sodium Malonic Ester.—In the introduction to this paper we have already mentioned the thorough work of Kohler and MacDonald¹ on the action of *p*-tolylsulfochloride on sodium malonic and acetoacetic esters. The action of phenylsulfochloride had not been tried, and, although this seemed hardly worth while, we thought an additional example of the hydrogen replacement would repay us for the slight amount of work involved. As we expected, we obtained sodium phenylsulfinate like Kohler and MacDonald, but unlike them, the product of the secondary reaction in our case was phenylsulfomalonic ester instead of the sulfoacetic ester obtained by them. This second product may be formed, as pointed out by Kohler and MacDonald, in two ways, either by some of the molecules of the sodium malonic ester giving the substituted malonic reaction, or by subsequent action between the sulfinate and the chloromalonic ester formed at first. That the second formation is the more probable they showed by carrying on this reaction between chloroacetoacetic ester and sodium *p*-tolylsulfinate, and in this case as in the primary reaction, obtained the *p*-tolylsulfoacetic ester instead of the acetoacetic ester;² whereas we, in a similar experiment with sodium phenylsulfinate and chloromalonic ester, obtained phenylsulfomalonic ester. These two differences between the results of Kohler and MacDonald, on the one hand, and ours, on the other, are obviously due to differences in the treatment. In the sulfochloride reaction the substituted malonic ester formed at first may have been decomposed because they dissolved it in water, and then evaporated the solution to dryness, whereas our product was made in the cold, and without exposing it to water. On the other hand, in their chloroacetoacetic ester experiment the use of heat and water was avoided, so that here we can only suggest the standing for two weeks, as the cause of the conversion of the acetoacetic ester into the acetic ester, since, in our work, the reacting mixture was not allowed to stand, but was worked up at once.

Kohler and MacDonald in one of their experiments obtained from the tolylsulfochloride and sodium acetoacetic ester 70% of sulfinate and 22% of tolylsulfoacetic ester. These yields are explained by the precipitation

¹ *Am. Chem. J.*, 22, 232 (1899).

² This had been tried earlier by Otto, *Ber.*, 23, 736 (1900).

of the sodium sulfinate by the ether used in the solvent, thus removing it from the sphere of the reaction as fast as it was formed. The account of our own work follows:

Sodium malonic ester prepared from the sodium ethylate from 3.5 g. of sodium and 28 cc. of malonic ester, diluted with several volumes of ether, was treated with phenylsulfochloride diluted with 20 cc. of dry benzene and the same volume of dry ether. A heavy, white precipitate formed at once, but in order to be sure the reaction was complete, the mixture was allowed to stand in the cold for 10 days, during which time the sodium ethylate from about 3.5 g. of sodium was added gradually, until the odor of the sulfochloride had gone. The precipitate was then filtered out, and washed with several small portions of ether. As the washings evaporated, long, white needles were deposited which were proved to be ethanetetra-carboxylic ester by the melting point 75° (uncor.) instead of 76° , as this was not altered, when the specimen was mixed with one of known ethanetetra-carboxylic ester.

The white precipitate was heated for some time with absolute alcohol, and filtered hot, when the filtrate on cooling deposited a considerable amount of white microscopic rectangular plates, while different crystals were obtained from the filtrate, after it had been evaporated to a small volume. The rectangular plates nearly insoluble in cold absolute alcohol were dissolved in water, and treated with hydrochloric acid, when a white, cloudy precipitate was obtained, but without filtration the mixture was extracted with ether, which yielded crystals melting at 83° (uncor.) after one crystallization from hot water. Phenylsulfinic acid melts at $83-84^{\circ}$. Both the acid and its sodium salt gave a characteristic white, flocculent silver salt soluble in nitric acid or in ammonium hydroxide. There is no doubt, therefore, that the substance is sodium phenylsulfinate.

The salt soluble in cold absolute alcohol gave on analysis

Subs., 1.0463; Na_2SO_4 , 0.2533.

Calc. for $\text{C}_6\text{H}_5\text{SO}_2\text{CNa}(\text{CO}_2\text{C}_2\text{H}_5)_2$: Na, 7.14; found: Na, 7.84.

The salt is therefore the sodium phenylsulfomalonic ester, the somewhat high result being due to some sulfinate which had been separated from it only by one crystallization from absolute alcohol. The sodium salt of phenylsulfoacetic ester contains 9.20% of Na.

Action of Chloromalonic Ester on Sodium Phenylsulfinate.—When solutions of equivalent amounts of the two substances in absolute methyl alcohol were mixed, a heavy, white precipitate of sodium chloride was formed at once. The filtrate was treated with a solution of sodium hydroxide in absolute methyl alcohol, until barely alkaline to phenolphthalein, and then on evaporation furnished white crystals, which were analyzed without purification.

Subs., 0.6035; Na_2SO_4 , 0.1397.

Calc. for $\text{C}_6\text{H}_5\text{SO}_2\text{CNa}(\text{COOC}_2\text{H}_5)$: Na, 7.14; found: Na, 7.50.

The products of the reaction, therefore, are phenylsulfomalonic ester and sodium chloride.

Action of Sodium Malonic Ester on 1-Bromomercapto-2,4-dinitrobenzene.—The 1-bromo-2,4-dinitrobenzene (melting at 71° (uncor.), instead of 72°), was converted into 2,4-dinitrophenyldisulfide, which blackened at 245° and melted at 285° , and this is as near as can be expected to its decomposition point, given as 280° . A specimen of this suspended in carbon tetrachloride was mixed with bromine in the proportion of one molecule of each substance. In a short time the color of the bromine had nearly disappeared, when the precipitate was washed with carbon tetrachloride. As it was essentially insoluble in all organic solvents, we saw no means of purifying it, and therefore used it direct in our experiments, although an analysis gave 21.94% of bromine instead of 28.67 calculated for the bromomercaptan, showing that it contained a quantity of unchanged disulfide. It blackened at about 120° instead of at 245° , as it should if the disulfide, and was proved to be the bromomercaptan by boiling a little of it with water, when the filtrate gave a strong test for hydrobromic acid with silver nitrate. A purer product was obtained by longer standing with the bromine and greater care in drying the carbon tetrachloride, but too late for our experiments.

Sodium malonic ester was prepared by the action of sodium on malonic ester in ether, which had been carefully dried but not previously freed from alcohol, and mixed with 1-bromomercapto-2,4-dinitrobenzene, suspended in benzene in the proportion of one molecule of the latter to 2 of the former. The mixture turned red, and most of the solid went into solution, showing that a reaction had taken place, as the bromomercaptan is insoluble in all the solvents present. After standing two days the red color had changed to pale yellow, and a heavy precipitate had formed. The filtrate from this was shaken with dilute sulfuric acid, and on evaporation yielded a small quantity of yellow crystals, which melted at 130° (uncor.), after crystallization from a mixture of ether and alcohol;—1-mercapto-2,4-dinitrobenzene melts at 131° . The crystals dissolved in dilute sodium hydroxide, and were reprecipitated unaltered on acidification. There seems to be no doubt, therefore, that they were the mercaptan. We were unable to analyze our specimen at the time we made it, and when the opportunity came, it had decomposed, as shown by a rise of over 50° in the melting point, undoubtedly due to the partial conversion of the mercaptan into the disulfide.

The precipitate was extracted with various solvents in the hope of obtaining more of the mercaptan and the expected ethanetetra-carboxylic ester, but the oils obtained deposited no crystals even after standing for

6 months, so we have no evidence of the formation of the tetracarboxylic ester. The undissolved portion of the precipitate was essentially insoluble in all solvents, and we suppose it to be mostly 2,4-dinitrophenyldisulfide, although it melted in the neighborhood of 260° with decomposition instead of at 280° . We have not thought it worth while to try to determine the nature of this body more accurately, since, as already noted, our bromomercaptan contained an impurity of the disulfide, so that its presence cannot be used as a proof of the formation of the mercaptan, although there is no question much of the mercaptan would have been converted into it both by the action of unchanged bromomercaptan and by the oxidizing action of the air.

Benzoyliodide and Sodium Malonic Ester.—This action was studied, because, according to our theory, benzoyliodide might give, with sodium malonic ester, benzaldehyd in addition to benzoylmalonic ester, the only product obtained with the chloride and bromide, which contain more negative halogens, and although our experiments could not be brought to a definite conclusion, owing to lack of time, it seems worth while to give a brief account of them.

The benzoyliodide was prepared by the excellent method of Staudinger and Anthes,¹ consisting in the treatment of benzoylchloride with carefully dried hydriodic acid. They give no directions for drying the acid, and, as we found this not altogether simple, we give the results of our experience. At first we used phosphoric pentoxide tubes alone, but found they were incapacitated so quickly by the iodine present that we adopted instead the following arrangement, which proved satisfactory: The hydriodic acid made from iodine red phosphorus and water was passed through a trap consisting of a long slender bottle lying horizontally, which kept back most of the iodine; then through 3 tubes of phosphoric pentoxide, followed by a U-tube immersed in ice and calcium chloride and standing in a Dewar flask. This removed the last trace of the iodine, after which the gas passed through freshly distilled benzoylchloride in a flask protected from moisture by a phosphoric pentoxide tube. The action was continued until a solution of the issuing gas gave no test for hydrochloric acid. The benzoyliodide prepared in this way was colorless, but on exposure to the light soon turned brown from liberation of iodine. For this reason the flask containing the benzoylchloride was carefully screened from light throughout the operation, and the product was used at once, after having been freed from the excess of hydriodic acid by a stream of dry carbonic dioxide. As the presence of iodine would interfere with our experiment by forming ethanetettracarboxylic ester, we used only fresh, colorless specimens, thinking that this was safer than trying to remove the iodine from altered

¹ *Ber.*, 46, 1417 (1913).

specimens by means of mercury, as recommended by Staudinger and Anthes.

After treatment with sodium malonic ester the benzoyliodide gave as the principal product benzoylmalonic ester, but if the oil containing this was shaken with warm water, and the solution thus obtained mixed with an equal volume of glacial acetic acid, and treated with phenylhydrazine, a small quantity of solid was obtained, which, after crystallization from hot alcohol, showed the constant melting point 163° (uncor.). It was divided into 4 fractions by partial precipitation of the alcohol solution with water, all of which melted at 163° (uncor.), so that it seemed to be homogeneous. Benzylidenephénylhydrazone prepared from benzaldehyd in the same way melted at 158° (uncor.), and when mixed with our product melting at 163° , the mixture melted at 160° (uncor.). On the other hand, benzoylphenylhydrazid prepared from fresh benzoyliodide and phenylhydrazine and melting at 167° (uncor.), instead of 168° , gave with our product melting at 163° a mixture melting at $135-140^{\circ}$. This is strong evidence that benzaldehyd was present in the product from the action of benzoyliodide on sodium malonic ester, but it cannot be accepted without much more work, because the melting point of our product does not agree with that of benzylidenephénylhydrazone. It is, in fact, 7° higher than the one usually accepted— 156° , Behrend and Leuchs.¹ There is, however, some evidence that this melting point is too low. Reutt and Pawlewski² found $158-160^{\circ}$; and in the last edition of Richter's *Lexicon* it is given as 160° , but we have been unable to find whether this is founded on Reutt and Pawlewski's work, or is independent of it. The benzylidenephénylhydrazone prepared from benzaldehyd by our process also melts higher—at 158° (uncor.), so that more study of this melting point seems desirable, but even if the true melting point should prove to be 160° , it is still 3° below that of the product from benzoyliodide, and this discrepancy has prevented us from using this work in the discussion of our theory. We regret that the pressure of other researches has prevented us from giving further study to this subject. We could find no ethanetetra-carboxylic ester among the products, but a small amount of it remaining dissolved in the oil would have escaped identification.

Action of *p*-Nitrobenzoylchloride on Sodium Malonic Ester, $C_6H_4NO_2 \cdot COCH(COOC_2H_5)_2$.—Five g. of the chloride made from *p*-nitrobenzoic acid melting at 235° (uncor.), instead of 238° were mixed with 4.5 g. of malonic ester dissolved in dry ether, and the mixture was treated with an absolute alcohol solution of the sodium ethylate from 0.5 g. of sodium. A heavy, white precipitate formed at once, but, to complete the reaction, the mixture was allowed to stand for 4 days, after which the filtrate was

¹ *Ann.*, 257, 227.

² *Chem. Zentr.*, 1903, II, 1432.

shaken with dilute sulfuric acid, and allowed to evaporate. White needles were obtained in this way, which, after washing with a sodium carbonate solution, were recrystallized from hot methyl alcohol, until they showed the constant melting point 93° (uncor.). No *p*-nitrobenzaldehyd or ethanetetracarboxylic ester could be detected among the products of the reaction.

Subs., 0.2941; N_2 , 11.8 cc. at 18° and 765 mm.

Calc. for $C_8H_4NO_5COCH(COOC_2H_5)_2$: N, 4.53; found: N, 4.66.

Properties of *p*-Nitrobenzoylmalonic Ester.—It forms white needles from methyl alcohol, which melt at 93° (uncor.). It is easily soluble in ethyl alcohol, ether, chloroform, or acetone; slightly soluble in cold methyl alcohol, or ethyl acetate, easily soluble hot; essentially insoluble in water.

Action of Bromomethanetricarboxylic Ester on Sodium Malonic Ester.—The methanetricarboxylic ester used by us boiled between 140° and 143° at 20 mm., and was, therefore, essentially pure. It was mixed with bromine in the proportion of one molecule of each, and, as at first no action took place, the mixture was warmed on the steam bath, which started a vigorous reaction. This was controlled by cooling with running water or warming, until the color of the bromine had disappeared, when it was shaken with powdered sodium carbonate, and allowed to stand with it over night. In the morning its reaction was neutral, and it was distilled under diminished pressure, the fraction boiling at 168 – 170° at 20 mm. being retained for use.

Eleven grams of this bromomethanetricarboxylic ester were mixed with the sodium malonic ester from 12 g. of the ester and 1.6 g. of sodium in dry ether and benzene, that is, two molecules of the sodium malonic ester for each molecule of the bromine compound. The mixture, after standing for nine weeks, was filtered from the precipitate of sodium bromide, and shaken with 10 cc. of strong hydrochloric acid diluted with 100 cc. of water, the benzene layer washed with dilute sodium carbonate solution, and dried over calcium chloride. On evaporating off the solvents an oil was obtained, which soon deposited crystals identified as ethanetetracarboxylic ester by the melting point, which was unchanged when mixed with a quantity of the pure ester. The oil obtained from the mother liquors and drained from the crystals came over for the most part between 170° and 175° at 45 mm. Methanetricarboxylic ester should boil at about 172° at this pressure, and, as this fraction gave no test for bromine, there seems no doubt that it was the methanetricarboxylic ester. After this fraction had passed over, the temperature rose to 270° , and the distillate obtained crystallized on cooling, and was recognized as ethanetetracarboxylic ester by its melting point. The pure crystals of this substance from the original oil weighed 7.5 g., that is, 67% of the calculated amount. This yield would be somewhat increased by the amounts ob-

tained from the mother liquors and the higher fraction. Apparently no other products were formed.

Action of α -Bromodiphenylpropiophenone with Sodium Malonic Ester.

—This substance was prepared by the action of bromine on the saturated ketone obtained from benzalacetophenone and phenylmagnesium bromide. Sodium malonic ester was prepared by treating 8.8 g. of malonic ester with the sodium ethylate prepared from 1.27 g. of sodium. The amount of absolute alcohol was kept so low that the whole solidified. To this was then added 10 g. of the bromine compound dissolved in dry benzene. The proportion, therefore, was 2 molecules of the ester to each molecule of other reagent. The sodium malonic ester dissolved giving an orange solution, which, after the mixture had stood 2 hours, had deposited a heavy, white precipitate, but in order to be sure the reaction had run to an end, it was allowed to stand 3 weeks. The product was shaken out with dilute sulfuric acid, when the benzene layer on evaporation left an oil, which solidified on stirring. The white solid thus obtained after several crystallizations from alcohol melted at 93° (uncor.), instead of at 95° , the melting point of the ketone $(C_6H_5)_2CHCH_2COC_6H_5$ but, as a mixture of our product with the pure ketone melted at $93-94^{\circ}$, there can be no doubt it is this compound. The yield of substance melting at 93° was 6 g., that is, 76% of the theoretical, and, as this had been crystallized several times, the reaction for its formation must have run essentially quantitatively. The mother liquors from these crystals on concentration and standing over night yielded other crystals, which, after purification from hot ether, proved to be ethanetetra-carboxylic ester, of which 4.7 g. were obtained, that is, 54% of the theoretical yield, but this comparatively small amount was explained by obtaining from the mother liquor 2.5 g. of an oil, which was principally bromomalonic ester to judge from its smell.

Mr. J. B. Conant, of this laboratory, informs us that, when he treated α -bromo - 3 - bromo - 4 - methoxyphenylpropiophenone, $CH_3OC_6H_3BrCH_2CHBrCOC_6H_5$, with sodium malonic methylester, he obtained a small amount of the ethanetetra-carboxylic methylester, indicating a similar reaction in this case, although apparently a less complete one than with the substance studied by us.

Reactions with Derivatives of Methylmalonic Ester.—In his work on these compounds Bischoff¹ found that chlorine compounds gave, as a rule, ethanetetra-carboxylic ester, while the bromine compounds yielded ethylenetetra-carboxylic ester. In only one case did he obtain the ethane ether from a bromine compound (bromomalonic ester with sodium methylmalonic ester), and then it was mixed with the ethylene compound. On the other hand, the chlorine compounds could be made to yield the ethylene ester by carrying on the reaction in boiling xylene. This result suggested

¹ *Ber.*, 29, 1510, 1515 (1896).

the idea that the ethylene derivative owed its formation to the action of heat, but, as it was possible that instead its appearance indicated a different course of the reaction, we have repeated Bischoff's experiments with bromine and methyl compounds carrying on the work in the cold.

Five grams of bromomethylmalonic ester diluted with its own volume of dry benzene were added to a dry benzene solution of 15.8 g. of malonic ester previously treated with the sodium ethylate from 2.2 g. of sodium. After standing in the cold 3 weeks the product was shaken with dilute hydrochloric acid, and the benzene layer allowed to evaporate spontaneously, when it yielded 4.3 g. of ethanetetra-carboxylic ester, that is, 68% of the theory. We could find no trace of ethylenetetra-carboxylic ester, but there may have been some of it dissolved in the oil. In this case, however, the large yield of the ethane compound shows that the ethylene derivative could not have been formed in large quantity.

Five grams of methylmalonic ester and the sodium ethylate from 0.66 g. of sodium were dissolved in dry benzene, and added gradually to 34.3 g. of bromomalonic ester also dissolved in dry benzene. After standing in the cold for 3 weeks the product was worked up as in the previous experiment, yielding an oil, which deposited 0.9 g. of ethanetetra-carboxylic ester. This small yield was undoubtedly due to the solution of most of the product in the oil consisting of the excess of bromomalonic ester. No ethylenetetra-carboxylic ester was detected, and while it is possible that some of it was present in the oil, it could not have been the principal product, as in that case the crystals would have contained some of it.

It follows from our experiments that ethanetetra-carboxylic ester is the product, if the work is carried on in the cold, and that therefore the ethylenetetra-carboxylic ester obtained by Bischoff owed its origin to the fact that his preparations were carried on at the boiling point of absolute alcohol, or at that of xylene.

Although the action of picrylchloride on sodium malonic ester has been frequently studied¹ in this laboratory, and careful search has been made for trinitrobenzene in the reaction products, no trace of this substance has been detected, so that the reaction runs principally, if not exclusively, in the usual way. In the hope of a different result we have tried the action of picrylchloride on sodium methylmalonic ester, but could find no trace of trinitrobenzene or dimethylethanetetra-carboxylic ester. The principal product crystallized in flat straw-colored needles, and melted constant at 78–79°. We have no doubt that it was the trinitrophenylmethylmalonic ester, but it was so explosive that we did not succeed in getting a good analysis of it, and as the main object of this experiment had been obtained, we did not feel inclined to use up on a secondary point the large

¹ Jackson, Soch, *Am. Chem. J.*, 18, 133 (1896); Jackson, Phinney, *Ibid.*, 21, 418 (1899).

amount of time, which would have been necessary to establish the composition of this substance.

The action of sodium malonic ester was also tried with the following substances: Nitro- and dinitrobenzyl iodide, and the corresponding sulfo cyanates, triiodoresorcine and tetrabromoorthoquinone; but in each case the product was an unmanageable oil, from which our greatest efforts failed to isolate any definite compound. Diiodoacetylene gave no reaction with sodium malonic ester, whether the solvent was absolute alcohol, dry ether, or dry benzene. We add a few observations made in the course of this work.

***p*-Nitrobenzylsulfocyanate**, $C_6H_4NO_2CH_2SCN$.—This substance was prepared by Henry¹ in 1869, but, as he does not even give the melting point of it, we describe it more in detail. *p*-Nitrobenzyl chloride was mixed with potassium sulfo cyanate in acetone solution, and the filtrate from the potassium chloride, which precipitated at once, was washed with water and cooled alcohol, after which the residue was recrystallized from hot alcohol, until it showed the constant melting point, 85–86° (uncor.).

Subs., 0.2368; BaSO₄, 0.2863.

Calc. for $C_6H_4NO_2CH_2SCN$: S, 16.58; found, S, 16.61.

Properties of *p*-Nitrobenzylsulfocyanate.—It forms very pale yellowish, long needles or slender prisms, which melt at 85–86° (uncor.), and dissolve easily in acetone, chloroform, or ethylacetate; soluble in benzene; slightly soluble in cold, soluble in hot alcohol, methyl alcohol, or ether; soluble in cold, very soluble in hot glacial acetic acid; almost insoluble in cold, soluble in hot carbon tetrachloride; slightly soluble in carbon disulfide; insoluble in cold, slightly soluble in hot petroleum ether; insoluble in water.

2,4-Dinitrobenzylsulfocyanate, $C_6H_3(NO_2)_2CH_2SCN$.—This substance was prepared in the same way as the mononitro compound. It showed the constant melting point, 86–87° (uncor.). It is certainly strange that this should differ by only one degree, from the melting point (85–86°) of the mononitro compound. A mixture of the two melted at 58–60°.

Subs., 0.2390; BaSO₄, 0.2342.

Calc. for $C_6H_3(NO_2)_2CH_2SCN$: S, 13.39; found: S, 13.46.

Properties of 2,4-Dinitrobenzylsulfocyanate.—It forms pale yellowish, short prisms terminated at both ends by planes at a somewhat acute angle. It melts at 86–87° (uncor.). It is very soluble in acetone, chloroform, or ethyl acetate; soluble in benzene; slightly soluble in the cold, soluble hot in alcohol, methyl alcohol, or glacial acetic acid; slightly soluble in ether, or carbon disulfide; almost insoluble cold, slightly soluble hot in carbon tetrachloride; essentially insoluble in petroleum ether, or water. In general, it is slightly less soluble than the mononitro compound.

¹ Ber., 2, 638 (1869).

The best solvent for it is hot alcohol. Both these sulfocyanates should be handled with care, as they have an irritating action on the skin, which in extreme cases may cause serious poisoning.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]
**STUDIES IN ESTERIFICATION. VI. THE ESTERIFICATION OF
 BENZOIC ACID BY MERCAPTANS.**

BY L. S. PRATT AND E. EMMET REID.

Received May 8, 1915.

Introduction.

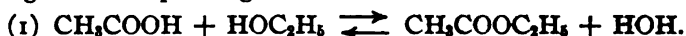
A study of the elements in any group of the periodic system reveals certain analogies and certain contrasts in their behavior. Both analogies and contrasts are found when we compare organic oxygen and sulfur derivatives.

One of the most studied organic reactions is that of esterification, while but little attention has been devoted to the esterification of any but oxygen alcohols.

The study of the esterification of sulfur alcohols was taken up in the hope of throwing light on the theory of esterification, and of comparing mercaptans, or sulfur alcohols, with oxygen alcohols.

Historical.

The classical experiments of Berthelot and Pean de St. Gilles,¹ and the more exact work of Menschutkin² and Lichty³ have shown that, when an alcohol is heated with an acid, esterification takes place and a well-defined limit is reached, and that the same limit may be reached by heating the corresponding ester with water.



The following values from the work of Menschutkin⁴ show the limits obtained by heating acetic acid and alcohols in equimolecular quantities, at 154°:

Methyl.....	69.52
Ethyl.....	66.57
Propyl.....	66.85
<i>n</i> -Butyl.....	67.30
<i>iso</i> -Butyl.....	67.38
Octyl.....	72.34
Cetyl.....	80.39

If these results are plotted as a curve, ethyl alcohol is found at the minimum, the limits increasing gradually with the molecular weights

¹ *Am. Chem. Pharm.*, [3] 65, 385-422 (1862); 66, 5-218 (1862); 68, 225-359 (1863).

² *Ber.*, 11, 1507 (1878); 10, 1728 (1877).

³ *Am. Chem. J.*, 17, 27 (1895); 18, 590 (1896).

⁴ *Ber.* 11, 1510 (1878).

of the alcohols. Methyl alcohol, however, instead of giving a limit below that reached by ethyl alcohol, shows a value corresponding roughly to that for heptyl alcohol. This is, however, in keeping with the usual abnormal behavior of the substance.

The effect of temperature on the limit of esterification has been the subject of considerable discussion, and even at the present time there is some uncertainty as to the facts in the case.

Menschutkin,¹ in 1884, quoted Berthelot as showing that no change in the limit of esterification is found with change in temperature, and confirmed this by his own results. However, he showed that in the case of amides the limit is considerably raised by elevation of temperature, while in the case of anilides, the limit decreases quite appreciably.

On the other hand, Sabatier and Maihle² quote the following values from the work of Berthelot, showing that the limit, in the esterification of acetic acid by ethyl alcohol, in equimolecular quantities, is not definitely fixed, but that it gradually changes with change in temperature:

Temperature.	Time.	Limit.
At room temperature	16 years	65.2%
100°	200 hours	65.6
170°	42 hours	66.5
200°	24 hours	67.3

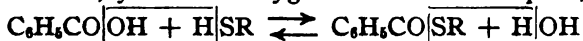
They confirm these by giving data, obtained with other alcohols and acids, at 280–300°, showing that at these temperatures the limits are appreciably higher than at lower temperatures.

It is an important and interesting fact that the limits, for various acids and many primary alcohols, obtained at the same temperature are all nearly alike, varying not widely from 66%.

Using benzoic acid and ethyl alcohol, Berthelot³ and Pean de St. Gilles obtained 66.5% as the limit, which is practically identical with the value 66.57% found by Menschutkin for acetic acid and ethyl alcohol.

Secondary and tertiary alcohols give widely different limits and here again it is found that alcohols of the same type give values which agree closely.

Reid,⁴ studying the mechanism of the reaction in esterification, employed mercaptans instead of alcohols, in order to distinguish between the (OH) or (SH) group of the acid and that of the alcohol. He showed, conclusively, that the (OH) group of the acid is eliminated with the (H) of the mercaptans as water, also that the reverse reaction, starting with the ester and water, yields the oxygen acid and mercaptan, as follows:



¹ *J. prakt. Chem.*, [2] 29, 437–47 (1884).

² *Compt. rend.*, 152, 495 (1911).

³ *Am. Chem. Pharm.*, [3] 68, 268 (1863).

⁴ *Am. Chem. J.*, 43, 489 (1910).

Reid also showed that the reaction reaches a well-defined limit, which confirms the original idea that mercaptans are true analogs of alcohols. He carried out a number of experiments, using benzoic acid with ethyl mercaptan, and found the limit to be at about 16.8%, which is much lower than the limit with alcohols. His work was preliminary, and his object was to establish the existence of the limit rather than to find its exact location. He did not extend the work to other mercaptans.

The present work was taken up to study more thoroughly the relations between mercaptans and alcohols, to determine whether the limits, for a series of mercaptans, follow relations observed with alcohols, and to discover, if possible, whether the limits are in any way dependent on temperature.

It should be pointed out that the difficulties encountered in this work are much greater than in the work with alcohols. In the latter case, Menschutkin, Berthelot and Pean de St. Gilles, and others, used constant proportions of alcohol and acid in a series. The mixture was prepared, and then definite amounts of it were sealed into the reaction tubes. Also, in analyzing the reaction mixture, the presence of alcohol need not be avoided. However, in working with mercaptans the proportions of active materials were widely varied, it being impossible to employ a mercaptan solution of the acid without very great loss due to the high vapor tensions of the mercaptans. Mercaptans, moreover, are acids, and can be titrated with alkali. Owing to this fact, it is necessary to eliminate the mercaptan from the reaction mixture before titration.

Such considerations make it evident that the experimental error in using mercaptans is larger than in using alcohols. On the other hand, there is a decided advantage in using varying proportions of active material, since systematic errors, which may become uniform and on that account escape notice, are thus avoided. The results obtained may not appear so accurate as those obtained by the other method, but they really mean more.

Materials.

Benzoic Acid.—The benzoic acid was a well-known firm's best grade.

Mercaptans.—The methyl and ethyl mercaptans were made by Reid for use in the work mentioned. Both were freed from sulfides, dried and distilled, only the best fractions being used in this work. The methyl mercaptan boiled at 6°, the ethyl at 35.5° to 36.1°.

The propyl, isobutyl and isoamyl mercaptans were standard commercial products.

The thiol esters were made by alkylating thiol-benzoic acid, prepared according to Kym's¹ general directions. The acid was, however, purified by dissolving the potassium salt in water, filtering, and liberating the

¹ *Ber.*, 32, 3533 (1899).

acid with HCl. After settling, the oily acid was separated and the aqueous solution extracted with ether. On evaporation of the ether, the acid was ready for use in making the esters.

Methyl Thiol-benzoate.—Dimethyl sulfate was used as the alkylating agent. 79 g. of thiol-benzoic acid were nearly neutralized with KOH solution. 79 g. of dimethyl sulfate were then added slowly with vigorous shaking, and cooling. The mixture was allowed to stand several hours, and was then heated two hours under a reflux condenser, the excess dimethyl sulfate being decomposed on boiling.

The ester separated from the solution and was removed by means of a separatory funnel. The solution was made alkaline and the remaining ester extracted with ether. The ester was washed several times with water, dried over CaCl_2 , the ether evaporated and the ester redistilled. The ester possessed a slight green color which, however, disappeared in several months, a faint brown color remaining. 50 g. of best fraction, b_p 134° was obtained, d_{25}^{25} 1.1381. Obermeyer¹ gives b_{760} 231–232°.

Ethyl Thiol-benzoate.—This was made according to the directions of Wheeler² from potassium thiol-benzoate and ethyl bromide. The ester was distilled in a partial vacuum. 31 g. of best fraction, b_p 146°, was obtained, having a faint brown color. The density found, d_{25}^{25} 1.0977, agrees well with the value found by Reid,³ d_{25}^{25} 1.0971, whose samples were fractionated at atmospheric pressure.

Propyl Thiol-benzoate.—This was made by the general method used by Wheeler⁴ in preparing the ethyl ester. The ester was carefully fractionated in a partial vacuum. 31 g. of best fraction, b_p 144°, were obtained. The density was found to be d_{25}^{25} 1.0724. The ester possessed a rather deep reddish brown color. Inasmuch as the method of preparation used was perfectly general, and well-known compounds employed, no analysis of the ester was made.

Water.—Conductivity water was used.

The Furnace.

An electric furnace (Fig. 1) was constructed as shown in the diagram. It consists of a brass tube, C, surrounded by a porcelain cylinder in two sections, B B', on which is wound the resistance wire.⁵ The system is insulated thermally by two inches of asbestos-magnesia steam-pipe packing, A A'. The electrical connections are so arranged as to allow the two electric units to be connected in parallel, in case more rapid heating is desired.

¹ Ber., 20, 2922 (1887).

² Am. Chem. J., 24, 69 (1900).

³ Ibid., 43, 493 (1910).

⁴ Loc. cit.

⁵ The ready wound porcelain cylinders were obtained from H. G. Crane, 226 Cypress St., Brookline, Mass.

One end of the brass tube rests against the adjustable set-screw D, which is placed in one end of the frame I. The other end presses against the short arm of the small lever E, the long arm of which acts against the short arm of the indicator lever F. The indicator lever is held in carefully adjusted cone bearings, H, which reduce friction to a minimum. The sliding contact between the two levers was worked very smooth and, when oiled, developed no appreciable friction. As the temperature rises, the brass tube expands, operates the system of levers

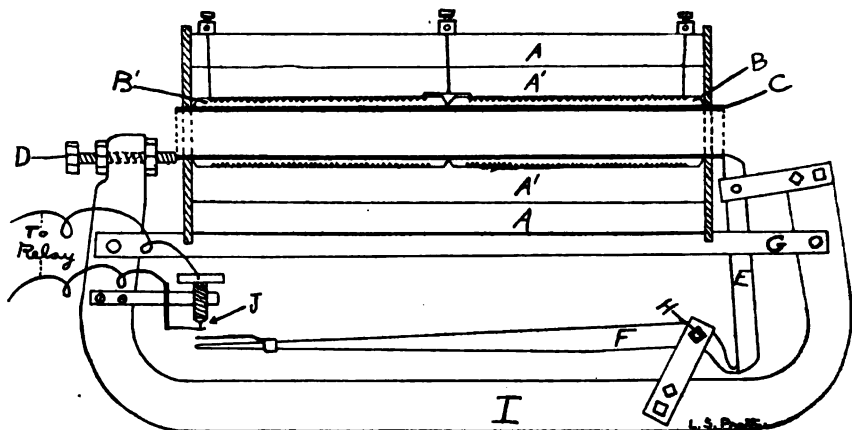


Fig. 1.

(which multiplies the motion about 100 times), and finally the strip of spring brass on the tip of the indicator lever closes the relay circuit by pressing the strip of platinum foil against the platinum point as shown in the apparatus J. The relay breaks the heating current, allowing the furnace to cool till the indicator lever drops slightly, opening the relay circuit. G is a bar to strengthen the frame. The furnace is set by inserting a thermometer in the end of the tube and adjusting the set-screw till the furnace regulates at the desired temperature.

When in operation, the brass tube is fitted at each end with asbestos plugs 1.5 inches thick, and covering the whole end is a raised plate of asbestos board, insulating from radiation, all points except the point of contact of the lever, or the set-screw, and the brass tube.

This furnace has given entire satisfaction, its performance being reproduceable after long periods of inactivity. It has been used at 193°, 220°, 243°, 270° and 300°. The temperature remained constant within a range of about 4°, which was sufficient for this work. Much of the variation is due to the time necessary for heat to penetrate the porcelain cylinders, which are about one-third of an inch thick.

Another furnace of somewhat similar design is in process of construc-

tion, employing alundum cylinders instead of porcelain, and affording better insulation, particularly at the ends of the tube. It is hoped that this furnace will maintain the temperature constant within 1° .

Standard Solutions.

The standard barium hydroxide was kept in a large stock bottle from which it was run through a siphon, with a stopcock, into the buret. The top of the buret and the stock bottle were protected from the carbon dioxide of the air by soda-lime tubes. The absence of any appreciable amount of BaCO_3 in the top of the buret, after five months' use of this apparatus, showed that the protection was adequate.

A similar system was used for the HCl solution, except that the vents were protected by tubes containing HCl solution.

Both solutions were approximately $0.1\text{ }N$, and were standardized frequently.

Procedure.

Hard glass tubes about $6 \times 75\text{ mm.}$, closed at one end, were boiled for six hours in dilute HCl , one hour in distilled water, and then thoroughly dried.

Acid Series.—Each tube was weighed, partly filled with benzoic acid, drawn out to a narrow neck and weighed again. The mercaptan was then introduced, the tube being cooled in ice and salt, and the tube sealed. The tube and the tip were then weighed.

Ester Series.—Each tube was weighed, partly filled with thiol-ester, drawn out and weighed again. One or two small drops of very pure water were then added and the tube sealed. The tube and the tip were then weighed. After being heated sufficiently in the furnace, and cooled, the tubes were ready for analysis. A tube was scratched with a file, kept for a time in a test-tube surrounded with ice and salt, to reduce pressure due to the vapor tension of the mercaptan, quickly broken, and the parts dropped into a 120 cc. Erlenmeyer flask. About 20 cc. of alcohol (distilled from KOH) were added to dissolve the reaction mixture.

The mercaptan was then "blown off" by passing a current of air (free from CO_2) through the solution for fifteen minutes, the solution being heated by immersing the flask in a large beaker of water kept at 50° .

The benzoic acid in the solution was then titrated with standard $\text{Ba}(\text{OH})_2$ solution using alcoholic phenolphthalein as indicator. This method of procedure was the result of a large amount of preliminary work testing the methods best adapted to eliminate or minimize the sources of error in each operation. It was tested by subjecting weighed amounts of benzoic acid, with and without added mercaptan, to the same treatment and then titrating. Correct results were thus obtained.

Experimental.

Since,¹ according to the usual reasoning in the consideration of reversible reactions, the amount of ester formed in unit time is equal to (benzoic acid) (mercaptan) K , and the amount of ester decomposed in the same time is equal to (water) (ester) K' (the expressions in parentheses represent concentrations), and since, at equilibrium, these opposing velocities are equal, we have:

$$\frac{(\text{Benzoic acid}) (\text{Mercaptan})}{(\text{Water}) (\text{Ester})} = \frac{K'}{K} = r$$

For equal concentrations of acid and mercaptan at equilibrium,

$$\frac{\text{Amount of mixture unesterified}}{\text{Amount of mixture esterified}} = \frac{\sqrt{K'}}{\sqrt{K}} = \frac{\sqrt{r}}{1}$$

or

$$\frac{\text{Amount of mixture esterified}}{1} = \frac{100}{\sqrt{r} + 1}^2$$

In percentages this becomes:

$$\text{Percentage of mixture of equivalent amounts, esterified at limit,} = \frac{100}{\sqrt{r} + 1}$$

This value is given in the last line in the following tables.

Preliminary experiments were carried out to determine the temperatures to be used, and the time necessary for the reactions to reach equilibrium. The results obtained for short periods of time were irregular and are not included in the tables, but the average results are of some interest and are plotted below in the form of a curve (Fig. 2). The temperature is not accurately known, as the thermometer used in setting the furnace was later found to be defective; but it was about 200°. The curve shows, roughly, the decrease in velocity as the reactions approach equilibrium.

Series I, II, III and IV are represented complete in tabular form, the methyl, ethyl, propyl, isobutyl and isoamyl series being arranged in the order named.

In tabulating the results, the data involved are arranged as follows:

- a, Acid or ester in grams.
- b, Millimols of acid or ester.
- c, Mercaptan or water in grams.
- d, Millimols of mercaptan or water.
- e, Cubic centimeters of alkali (0.09210 *N*) required for titration.
- f, Millimols of acid present calculated from e. In ester series this equals mercaptan.

¹ Reid, *Am. Chem. J.*, 43, 499 (1910); see also Bonz, *Z. physik. Chem.*, 2, 865 (1888).

² By a typographical error, this is printed in Reid's paper as $100/\sqrt{r} - 1$, but his results were all calculated by the correct formula.

g, Millimols mercaptan remaining (in acid series).

h, Millimols ester remaining (in ester series).

k, Millimols water = remaining (in ester series).

m, Millimols ester = water (in acid series).

%, percentage esterification. This is calculated, by formula deduced above, for equivalent concentrations of acid and mercaptan or ester and water.

In acid series, in which the start is made with acid and mercaptan, the amount of ester given (*m*) is found by subtracting the acid remaining (*f*) from (*b*) the original acid. The concentration of ester (*m*) equals

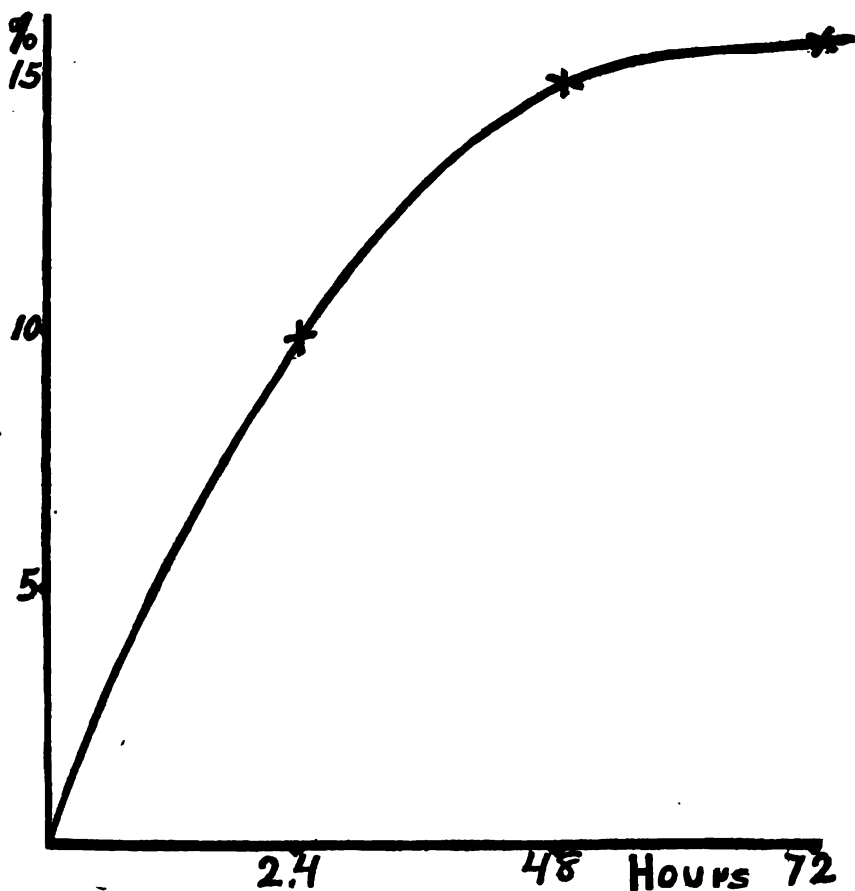


Fig. 2.

the concentration of water. The millimols of mercaptan remaining, as given in (*g*), is obtained by subtracting the amount of ester (*m*) from (*d*) the mercaptan originally present.

In the ester series, starting with ester and water, the amount of ester given (h) is found by subtracting the acid present (f) from (b) the original ester. The water remaining (k) is obtained by subtracting the acid present (f) from (d) the original water.

All the figures given, except those represented by a , c , e , \sqrt{r} and $\%$, are in millimols.

The tables for corresponding acid and ester series are lettered as follows: Acid series A, B, etc., ester series A', B', etc.

Bracketed results are not used in calculating the limits.

TABLE A.— $C_6H_5COOH + CH_3SH$.
67 hours at 193° and 168 hours at 243° .

$a \dots$	0.1429	0.1268	0.1344	0.1463	0.1543	0.1581	0.1470	0.1391	0.1840	0.1891
$b \dots$	1.1707	1.0389	1.1012	1.1986	1.2642	1.2953	1.2044	1.1396	1.5076	1.5493
$c \dots$	0.1484	0.0573	0.1746	0.0765	0.0847	0.0556	0.1301	0.0532	0.1485	0.0917
$d \dots$	3.0851	1.1912	3.6298	1.5904	1.7609	1.1558	2.7048	1.1060	3.0873	1.9065
$e \dots$	8.75	8.88	7.90	10.09	10.50	11.51	9.36	10.04	11.88	13.23
$f \dots$	0.8059	0.8178	0.7276	0.9293	0.9670	1.0601	0.8621	0.9247	1.0942	1.2185
$g \dots$	2.7203	0.9701	3.2562	1.3211	1.4637	0.9206	2.3625	0.8911	2.6739	1.5757
$m \dots$	0.3648	0.2211	0.3736	0.2693	0.2972	0.2352	0.3423	0.2149	0.4134	0.3308
$\sqrt{r} \dots$	4.0588	4.0285	4.1199	4.1144	4.0030	4.2002	4.1692	4.2240	4.1375	4.1887
$\% \dots$	19.8	19.9	19.6	19.6	20.0	19.2	19.3	19.2	19.4	19.3

Average, 19.5%.

TABLE A'.— $C_6H_5COSCH_3 + H_2O$.
67 hours at 193° and 168 hours at 243° .

$a \dots$	0.3442	0.2888	0.2534	0.2911	0.2618	0.2709	0.2924	0.2647	0.2915	0.2933
$b \dots$	2.2644	1.9000	1.6671	1.9152	1.7224	1.7822	1.9238	1.7414	1.9178	1.9296
$c \dots$	0.0512	0.0571	0.0551	0.0375	0.0485	0.0490	0.0508	0.0445	0.0566	0.0836
$d \dots$	2.8441	3.1718	3.0607	2.0831	2.6941	2.7220	2.8219	2.4720	3.1442	4.6440
$e \dots$	21.60	19.02	16.78	17.64	17.13	17.68	18.95	17.08	19.25	19.93
$f \dots$	1.9894	1.7517	1.5454	1.6246	1.5777	1.6284	1.7453	1.5731	1.7729	1.8355
$h \dots$	0.2750	0.1483	0.1217	0.2906	0.1447	0.1538	0.1785	0.1683	0.1449	0.0941
$k \dots$	0.8547	1.4201	1.5153	0.4585	1.1164	1.0936	1.0766	0.8989	1.3713	2.8085
$\sqrt{r} \dots$	4.1034	3.8172	3.5987	4.4508	3.9254	4.3423	3.9813	4.0445	3.9772	3.5704
$\% \dots$	19.6	20.7	21.7	18.3	20.3	18.7	20.0	19.8	20.0	21.9

Average, 20.1%. Limit from A and A', 19.6%.

TABLE B.— $C_6H_5COOH + CH_3SH$.
168 hours at 220° .

$a \dots$	0.1527	0.1394	0.1325	0.1485	0.1369	0.1481
$b \dots$	1.2511	1.1421	1.0856	1.2167	1.1216	1.2134
$c \dots$	0.1939	0.1875	0.1233	0.1182	0.1633	0.1506
$d \dots$	4.0312	3.8981	2.5634	2.4574	3.3950	3.1310
$e \dots$	9.23	8.30	8.42	9.73	8.37	9.38
$f \dots$	0.8501	0.7644	0.7755	0.8961	0.7709	0.8639
$g \dots$	3.6302	3.5204	2.2533	2.1368	3.0443	2.7816
$m \dots$	0.4010	0.3777	0.3101	0.3206	0.3507	0.3495
$\sqrt{r} \dots$	4.4317	4.3431	4.2629	4.3162	4.3682	4.4353
$\% \dots$	18.4	18.7	19.0	18.8	18.6	18.4

Average, 18.6%.

TABLE B.— $C_6H_5COSCH_3 + H_2O$.
168 hours at 220°.

a.....	0.2923	0.1887	0.2192	0.2756	0.2413	0.3137
b.....	1.9230	1.2414	1.4421	1.8132	1.5875	2.0638
c.....	0.0776	0.0532	0.0341	0.0338	0.0291	0.0436
d.....	4.3106	2.9552	1.8942	1.8776	1.6165	2.4220
e.....	19.80	12.91	14.00	16.60	14.52	19.60
f.....	1.8236	1.1890	1.2894	1.5289	1.3373	1.8052
h.....	0.0994	0.0524	0.1527	0.2843	0.2502	0.2586
k.....	2.4870	1.7662	0.6048	0.3487	0.2792	0.6168
\sqrt{r}	3.6677	3.9084	4.2430	4.8558	5.0597	4.5200
%.....	21.4	20.4	19.1	17.1	16.5	18.2

Average, 18.8%. Limit from B and B', 18.7%.

TABLE C.— $C_6H_5COOH + C_2H_5SH$.
240 hours at 193° and 168 hours at 243°.

a....	0.1425	0.1770	0.2002	0.1827	0.2179	0.1559	0.2068	0.1986	0.1718
b....	1.1675	1.4502	1.6403	1.4969	1.7853	1.2773	1.6944	1.6272	1.4076
c....	0.1555	0.1257	0.0818	0.1186	0.1530	0.1644	0.1128	0.1079	0.1040
d....	2.5036	2.0238	1.3170	1.9095	2.4634	2.6470	1.8161	1.7372	1.6744
e....	9.91	12.94	15.35	13.51	15.97	10.96	15.54	14.94	12.77
f....	0.9127	1.1917	1.4137	1.2443	1.4708	1.0094	1.4312	1.3760	1.1761
g....	2.2488	1.7653	1.0904	1.6569	2.3791	2.3791	1.5529	1.4860	1.4429
h....	0.2548	0.2585	0.2266	0.2526	0.3145	0.2679	0.2632	0.2512	0.2315
\sqrt{r} ..	5.6226	5.6110	5.4793	5.6844	5.9193	5.7844	5.6640	5.6925	5.6273
%...	15.1	15.1	15.4	15.0	14.4	14.7	15.0	14.9	15.1

Average, 15.0%. Traces of H_2S .TABLE C'.— $C_6H_5COSC_2H_5 + H_2O$.
240 hours at 193° and 168 hours at 243°.

a....	0.3377	0.3538	0.3492	0.3580	0.3416	0.3232	0.2807	0.3695	0.3454	0.3815
b....	2.0343	2.1313	2.1036	2.1566	2.0578	1.9470	1.6910	2.2259	2.0807	2.2982
c....	0.0606	0.0519	0.0682	0.0795	0.0544	0.0386	0.0623	0.0560	0.1335	0.0536
d....	3.3663	2.8830	3.7885	4.4162	3.0220	2.1443	3.4607	3.1108	7.4159	2.9774
e....	20.76	21.36	21.59	22.09	20.75	18.78	17.54	22.25	21.68	22.95
f....	1.9120	1.9673	1.9884	2.0345	1.9111	1.7297	1.6154	2.0492	1.9967	2.1137
h....	0.1223	0.1640	0.1152	0.1221	0.1467	0.2173	0.0756	0.1767	0.0840	0.1845
k....	1.4543	0.9157	1.8001	2.3817	1.1109	0.4146	1.8453	1.0616	5.4192	0.8637
\sqrt{r} ..	4.5336	5.0764	4.3665	3.7727	4.7340	5.7627	4.3248	4.7312	9.3585	5.2950
%..	18.1	16.4	18.6	20.9	17.5	(14.8)	18.8	17.5	(9.6)	15.9

Average, 18.0%. Limit from C and C', 15.4%. Traces of H_2S .

TABLE D.— $C_6H_5COOH + C_2H_5SH$.
96 hours at 220°.

a	0.2209	0.1613	0.1564	0.1673
b	1.8099	1.3215	1.2814	1.3707
c	0.1668	0.1647	0.1360	0.1374
d	2.6856	2.6517	2.1896	2.2122
e	16.19	11.39	11.30	12.14
f	1.4911	1.0490	1.0407	1.1181
g	2.3668	2.3792	1.9489	1.9596
m	0.3188	0.2725	0.2407	0.2526
\sqrt{r}	5.8927	5.7974	5.9167	5.8600
%	14.5	14.7	14.5	14.6

Average, 14.6%.

TABLE E.— $C_6H_5COOH + C_2H_5SH$.
168 hours at 220°.

0.1818	0.1756	0.2310	0.1873	0.1783	0.2052
1.4895	1.4387	1.8926	1.5446	1.4608	1.6813
0.1205	0.1166	0.1395	0.1259	0.1438	0.1354
1.9402	1.8773	2.2460	2.0271	2.3153	2.1800
13.51	13.06	17.38	13.98	13.06	15.33
1.2443	1.2028	1.6007	1.2875	1.2028	1.4119
1.6950	1.6414	1.9541	1.7700	2.0573	1.9106
0.2452	0.2359	0.2919	0.2571	0.2580	0.2694
5.9229	5.9564	6.0588	5.8719	6.0971	6.0965
14.5	14.4	14.2	14.6	14.1	14.1

Average, 14.3%.

TABLE D'.— $C_6H_5COSC_2H_5 + H_2O$.
96 hours at 220°.

a	0.2752	0.2884	0.2980	0.2828
b	1.6578	1.7374	1.7952	1.7036
c	0.0496	0.0314	0.0267	0.0330
d	2.7553	1.7842	1.4832	1.8331
e	16.59	15.93	14.86	15.98
f	1.5280	1.4672	1.3685	1.4717
h	0.1298	0.2702	0.4267	0.2319
k	1.2273	0.2770	0.1147	0.3614
\sqrt{r}	3.8284	5.3630	6.1861	5.0837
%(20.7)	15.7	(13.9)	16.4	

Average, 16.1%. Limit from D and D', 14.8%.

TABLE E'.— $C_6H_5COSC_2H_5 + H_2O$.
168 hours at 220°.

0.2310	0.3104	0.2468	0.2963	0.2489	0.3043
1.3915	1.8698	1.4867	1.7849	1.4994	1.8331
0.0330	0.0484	0.0259	0.0323	0.0379	0.0385
1.8331	2.6886	1.4387	1.7942	2.1054	2.1386
13.71	18.55	13.55	16.60	14.92	17.66
1.2626	1.7084	1.2480	1.5289	1.3741	1.6265
0.1289	0.1614	0.2387	0.2560	0.1253	0.2066
0.5705	0.9802	0.1907	0.2653	0.7313	0.5121
4.6561	4.2952	5.8427	5.8666	4.5393	5.0004
17.7	18.8	14.6	14.6	18.0	16.7

Average, 16.7%. Limit from E and E', 14.6%.

TABLE F.— $C_6H_5COOH + C_2H_5SH$.
240 hours at 193° and 168 hours at 243°.

a	0.2080	0.1813	0.1951	0.1615	0.2090	0.1885	0.1466
b	1.7042	1.4854	1.5621	1.3232	1.7124	1.5444	1.2011
c	0.0523	0.0789	0.0755	0.0754	0.0794	0.0826	0.0823
d	0.6870	1.0364	0.9917	0.9904	1.0429	1.0849	1.0810
e	16.76	14.15	15.28	12.50	16.44	14.70	11.24
f	1.5436	1.3032	1.4073	1.1512	1.5141	1.3538	1.0352
g	0.5264	0.8542	0.8369	0.8184	0.8446	0.8943	0.9151
m	0.1606	0.1822	0.1548	0.1720	0.1983	0.1906	0.1659
\sqrt{r}	5.6128	5.7907	7.0104	5.6432	5.7026	5.7730	5.7333
%	15.1	14.7	(12.5)	15.1	14.9	14.8	14.9

Average, 14.9%. Traces of H_2S .

TABLE F'.— $C_6H_5COSC_6H_7 + H_2O$.
240 hours at 193° and 168 hours at 243°.

a.....	0.3123	0.2846	0.2963	0.3028	0.2910	0.2121	0.2797
b.....	1.7350	1.5811	1.6461	1.6822	1.6167	1.1783	1.5539
c.....	0.0462	0.0588	0.0552	0.0621	0.0441	0.0189	0.0507
d.....	2.5664	3.2663	3.0663	3.4497	2.2498	1.0498	2.8164
e.....	17.76	16.55	17.17	17.54	16.48	10.41	16.18
f.....	1.6357	1.5243	1.5814	1.6154	1.5178	0.9588	1.4902
h.....	0.0993	0.0568	0.0647	0.0668	0.0989	0.2195	0.0637
k.....	0.9307	1.7420	1.4849	1.8343	0.7320	0.0910	1.3262
\sqrt{r}	5.3805	4.8459	5.1018	4.6147	5.6410	6.7840	5.1271
%.....	15.7	17.1	16.4	17.8	15.1	(12.9)	16.3

Average, 16.4%. Limit from F and F', 15.1%. Traces of H_2S .

TABLE G.— $C_6H_5COOH + C_6H_7SH$.
168 hours at 220°.

a	0.1946	0.2266	0.2216	0.1634	0.1625	0.1863	0.2186	0.1997	0.1913
b	1.5944	1.8566	1.8156	1.3387	1.3314	1.5264	1.7910	1.6362	1.5674
c	0.1302	0.1074	0.2436	0.1202	0.1038	0.1654	0.0627	0.0860	0.0443
d	1.7102	1.4107	3.1998	1.5788	1.3634	2.1726	0.8236	1.1296	0.5819
e	14.83	17.67	16.22	12.38	12.40	13.94	17.63	15.66	15.57
f	1.3658	1.6274	1.4938	1.1402	1.1420	1.2838	1.6237	1.4423	1.4340
g	1.4816	1.1815	2.8780	1.3803	1.1740	1.9300	0.6563	0.9357	0.4485
m	0.2286	0.2292	0.3218	0.1985	0.1894	0.2646	0.1673	0.1939	0.1334
\sqrt{r}	6.2228	6.0500	6.4433	6.3200	6.1135	6.4887	6.1701	5.9913	6.0115
%	13.9	14.2	13.4	13.7	14.1	13.4	13.9	14.3	14.2

Average, 13.8%. Traces of H_2S .

TABLE H.— $C_6H_5COOH + C_6H_7SH$.
240 hours at 193°.

a	0.1946	0.2266	0.2216	0.1634	0.1625	0.1863	0.2186	0.1997	0.1913
b	1.5944	1.8566	1.8156	1.3387	1.3314	1.5264	1.7910	1.6362	1.5674
c	0.1302	0.1074	0.2436	0.1202	0.1038	0.1654	0.0627	0.0860	0.0443
d	1.7102	1.4107	3.1998	1.5788	1.3634	2.1726	0.8236	1.1296	0.5819
e	14.83	17.67	16.22	12.38	12.40	13.94	17.63	15.66	15.57
f	1.3658	1.6274	1.4938	1.1402	1.1420	1.2838	1.6237	1.4423	1.4340
g	1.4816	1.1815	2.8780	1.3803	1.1740	1.9300	0.6563	0.9357	0.4485
m	0.2286	0.2292	0.3218	0.1985	0.1894	0.2646	0.1673	0.1939	0.1334
\sqrt{r}	6.2228	6.0500	6.4433	6.3200	6.1135	6.4887	6.1701	5.9913	6.0115
%	13.9	14.2	13.4	13.7	14.1	13.4	13.9	14.3	14.2

Average, 14.1%.

TABLE G'.— $C_6H_5COSC_6H_7 + H_2O$.
168 hours at 220°.

a	0.3185	0.2992	0.2333	0.3138	0.2452	0.2431	0.2694	0.3268	0.2817
b	1.7694	1.6622	1.2961	1.7433	1.3622	1.3505	1.4966	1.8155	1.5650
c	0.0456	0.0642	0.0511	0.0255	0.0357	0.0320	0.0466	0.0648	0.0596
d	2.5330	3.5663	2.8386	1.4165	1.9832	1.7776	2.5886	3.5996	3.3108
e	18.08	17.44	13.60	14.54	13.93	13.64	15.56	18.98	16.45
f	1.6652	1.6062	1.2525	1.3391	1.2829	1.2562	1.4331	1.7481	1.5151
h	0.1042	0.0560	0.0436	0.4042	0.0793	0.0943	0.0635	0.0674	0.0499
k	0.8678	1.9601	1.5861	0.0774	0.7003	0.5214	1.1555	1.8515	1.7957
\sqrt{r}	5.5375	4.8480	4.7630	7.5707	5.4443	5.6653	5.2905	5.5522	5.0613
%	15.3	17.1	17.4	(11.7)	15.5	15.0	15.9	15.3	16.5

Average, 16.1%. Limit from G and G', 14.1%. Traces of H_2S .

TABLE H'.— $C_6H_5COSC_6H_7 + H_2O$.
240 hours at 193°.

a	0.3185	0.2992	0.2333	0.3138	0.2452	0.2431	0.2694	0.3268	0.2817
b	1.7694	1.6622	1.2961	1.7433	1.3622	1.3505	1.4966	1.8155	1.5650
c	0.0456	0.0642	0.0511	0.0255	0.0357	0.0320	0.0466	0.0648	0.0596
d	2.5330	3.5663	2.8386	1.4165	1.9832	1.7776	2.5886	3.5996	3.3108
e	18.08	17.44	13.60	14.54	13.93	13.64	15.56	18.98	16.45
f	1.6652	1.6062	1.2525	1.3391	1.2829	1.2562	1.4331	1.7481	1.5151
h	0.1042	0.0560	0.0436	0.4042	0.0793	0.0943	0.0635	0.0674	0.0499
k	0.8678	1.9601	1.5861	0.0774	0.7003	0.5214	1.1555	1.8515	1.7957
\sqrt{r}	5.5375	4.8480	4.7630	7.5707	5.4443	5.6653	5.2905	5.5522	5.0613
%	15.3	17.1	17.4	(11.7)	15.5	15.0	15.9	15.3	16.5

Average, 15.6%. Limit from H and H', 14.3%.

TABLE I.— $C_4H_7COOH + Me_3CH.CH_2SH$.

67 hours at 193° and 168 hours at 243°.

a...	0.1458	0.1341	0.1923	0.1562	0.1680	0.1701	0.1953	0.1519	0.1876	0.1849
b...	1.1945	1.0987	1.5756	1.2797	1.3764	1.3936	1.6002	1.2445	1.5379	1.5150
c...	0.0717	0.0818	0.0872	0.0596	0.1098	0.0832	0.0989	0.1664	0.1157	0.1221
d...	0.7953	0.9073	0.9672	0.6611	1.2178	0.9228	1.0969	1.8456	1.2832	1.3543
e...	11.58	10.48	15.43	12.70	13.25	13.52	15.43	11.61	15.00	14.54
f...	1.0665	0.9652	1.4211	1.1696	1.2203	1.2452	1.4211	1.0692	1.3815	1.3391
g...	0.6673	0.7738	0.8127	0.5510	0.0617	0.7744	0.9178	1.6703	1.1268	1.1784
m...	0.1280	0.1335	0.1545	0.1101	0.1561	0.1484	0.1791	0.1753	0.1564	0.1759
\sqrt{r}	6.5907	6.4733	6.9557	7.2914	7.2919	6.6172	6.3765	7.6234	7.9776	7.1414
%...	13.2	13.4	12.6	12.1	12.1	13.1	13.5	11.6	11.1	12.3

Average, 12.5%. Traces of H_2S . Limit, 12.7%.TABLE I'.— $C_4H_7COOH + Me_3CH.CH_2CH_2SH$.

67 hours at 193° and 168 hours at 243°.

a...	0.1909	0.1776	0.1925	0.2190	0.2139	0.1896	0.2319	0.1662	0.2354	0.1727
b...	1.5641	1.4551	1.5772	1.7943	1.7526	1.5534	1.9000	1.3617	1.9287	1.4150
c...	0.1022	0.0957	0.1394	0.0802	0.1107	0.0794	0.1271	0.0766	0.1126	0.1461
d...	0.9812	0.9188	1.3383	0.7700	1.0627	0.7623	1.2202	0.7354	1.0810	1.4026
e...	13.25	12.31	12.53	16.42	15.03	13.77	16.12	12.11	16.90	10.65
f...	1.2203	1.1337	1.1540	1.5123	1.3842	1.2682	1.4846	1.1153	1.5565	0.9809
h...	0.6374	0.5974	0.9151	0.4880	0.6943	0.4771	0.8048	0.4890	0.7088	0.9685
k...	0.3438	0.3124	0.4232	0.2820	0.3684	0.2852	0.4144	0.2464	0.3722	0.4341
\sqrt{r}	8.1120	8.0974	7.6787	9.6333	8.4152	8.6247	8.3210	9.4779	8.9239	7.1002
%...	11.0	11.0	11.5	9.4	10.6	10.4	10.7	9.5	10.1	12.3

Average, 10.6%. Traces of H_2S . Limit, 10.8%.

Discussion of Results.

On examination of the foregoing results, it is evident that, while very concordant values are obtained from the acid series, those obtained from the ester series show wide variations. This was noted early in the work, and an attempt was made to discover the reason. Great care was exercised in the preparation of the tubes, and in some of the later work the furnace was rocked frequently to insure more thorough mixing in the tubes, but the variations were not eliminated. This feature of the problem will be investigated further.

It is evident that in all of the series the reaction nearly reached the limit, the values from acid and ester series differing in most cases by less than 2%. This is especially important in considering the isobutyl and isoamyl series, inasmuch as in these cases no ester series was run. However, since in the other series, heated the same length of time at the same temperature, the reaction went nearly to the limit, it is reasonable to assume that in these series also the limit was very nearly reached. On this assumption, the limits for these two series are set fairly definitely.

One point of particular interest, as shown more clearly in the table below which sums up all the results, is in regard to the relative stability of the esters, inasmuch as it is believed from this work that the ester is the substance which undergoes decomposition. It will be noted that no decomposition was detected in the tubes containing methyl esters at 243°. In the case of the ethyl ester slight decomposition was found in tube heated at 243°, but none in tubes heated at 220°, while in the case of the propyl ester slight decomposition was found at 220°. It should be stated that only slight traces of H_2S were found in tubes heated at any temperature below 270°, but at this temperature, in the ethyl series, decomposition took place to an extent that completely vitiated the results. The values obtained were not tabulated.

It appears, from these facts, that the stability of the esters, in this homologous series, decreases steadily with increase in molecular weight. In a series of six tubes heated at 300°, five exploded, and the contents of the sixth showed very strong decomposition, being nearly black. As pointed out in the introduction, the limits reached in a homologous series of alcohols may be plotted in a curve, with ethyl alcohol at the minimum, the limits ascending with increase in molecular weight, on the one hand, and methyl alcohol reaching an abnormally high limit, on the other. The results for various mercaptans tabulated below, Table J, show that with the mercaptans the limit is higher for methyl than for ethyl, but the limit, instead of rising for higher molecular weights, seems to decrease slightly.

The isobutyl and isoamyl limits can hardly be plotted as representative of higher molecular weights in this connection, as forked-chain compounds are not strictly comparable to normal compounds.

TABLE J.—LIMITS AT VARIOUS TEMPERATURES WITH VARIOUS MERCAPTANS.

Temperature.	Methyl.	Ethyl.	Propyl.	Isobutyl.	Isoamyl.
193°	14.3
220°	18.7	14.7	14.1 ¹
243°	19.6	15.4 ¹	15.1 ¹	12.7 ¹	10.8 ¹
270° ²
300° ³

The data are not extensive enough to show conclusively the influence of temperature on the limit, but so far as the observations go, the limits are higher for higher temperatures, the elevation being of the same order and in the same direction as in the results quoted for the alcohols.

By examining the data in the various tables it will be seen that the proportions of acid and mercaptan, or ester and water, used have no appreciable influence on the limit.

¹ Slight decomposition. Lead acetate papers showed trace of hydrogen sulfide.

² Considerable decomposition.

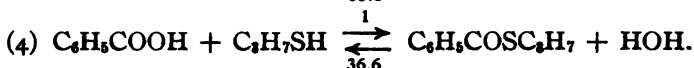
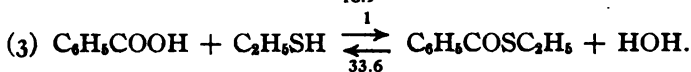
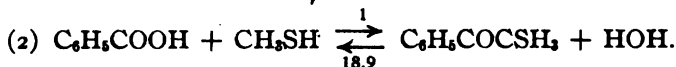
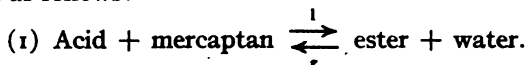
³ Complete decomposition.

Conclusions.

(1) It has been conclusively shown that the mercaptans are entirely analogous to the alcohols in esterification.

(2) The limits obtained, using mercaptans, follow, in general, relations observed using alcohols, but are much lower.

(3) The reactions between methyl, ethyl and propyl mercaptans and benzoic acid, and between the thiol-esters and water at 220° may be represented as follows:



(4) The stability of the esters was found to decrease with increase in molecular weight.

(5) The limit was found to be independent of the proportions of the reacting substances.

(6) The limits were found to ascend gradually with rise in temperature.

This work will be extended to other mercaptans and to other acids, and will include a study of secondary and tertiary mercaptans. The latter phase should prove to be of special interest on account of the relations observed using secondary and tertiary alcohols.

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PHENOLQUINOLINEIN, A HETEROCYCLIC ANALOG OF PHENOLPHTHALEIN.

By ARTHUR W. DOX.

Received June 19, 1915.

The similarity in behavior of quinolinic acid and phthallic acid was pointed out by Bernthsen and Mettegang¹ in 1887. These investigators showed that quinolinic anhydride reacts with benzene in the presence of aluminium chloride, according to the Friedel-Crafts reaction, to form benzoylpyridine carboxylic acid, just as phthallic acid under similar conditions yields benzoylbenzoic acid. They succeeded also in preparing a condensation product of quinolinic anhydride with resorcin, corresponding to fluorescein, which they named fluorazein. Like fluorescein it was strongly fluorescent, and on treatment with bromine it yielded an eosin-like dye.

¹ Ber., 20, 1208 (1887).

The writer thought it might be of interest to prepare the analog of phenolphthalein by condensing quinolinic anhydride with phenol, and to ascertain whether the resulting product would have the properties of an indicator.

Quinolinic acid was converted into its anhydride by heating with acetic anhydride and washing out the acetic acid and excess of acetic anhydride by means of carbon tetrachloride. Phillips¹ recommends heating one part of the acid with two parts of acetic anhydride to 120°, then gradually raising the temperature to 150°. The writer found that a quantitative yield of the anhydride was obtained by gently heating the mixture until solution was effected, then simply boiling for five minutes. On cooling, the anhydride separated out, and after washing with carbon tetrachloride, it showed the correct melting point of 134°.

Ten grams of quinolinic anhydride, 20 g. phenol, and 8 g. of concentrated sulfuric acid were heated in an oil bath at 120° for ten hours. The mixture was then poured into water, and the solution boiled until the excess of phenol was expelled. A yellow granular precipitate formed, which was collected on a filter, then dissolved in alcohol and purified by boiling with charcoal. A nearly colorless solution was obtained, which on evaporating and diluting with water became milky and finally yielded a yellowish granular sediment. The product was analyzed for nitrogen by the Kjeldahl-Gunning method.

Calc. for $C_{13}H_{11}NO_4$: N, 4.56; found, 4.50.

Like phenolphthalein, phenolquinolinein is a brilliant indicator, giving an intense pink color with alkalis which is immediately discharged on acidifying. On account of the basic nature of the pyridine nucleus, the end point might be expected to be somewhat different from that of phenolphthalein, but this was not determined. On account of the present cost of quinolinic acid, it is not probable that the indicator will find any extensive application in titrimetric work. The analogy, however, is considered of sufficient interest to warrant this brief paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

STUDIES ON THE CULTURE MEDIA EMPLOYED FOR THE BACTERIOLOGICAL EXAMINATION OF WATER.

II. LACTOSE-PEPTONE MEDIA.²

By E. M. CHAMOT AND C. M. SHERWOOD.

Received June 17, 1915.

The most important of all the qualitative methods for the bacteriological examination of water are unquestionably those in which advantage is

¹ *Ann.*, 288, 255 (1895).

² Read at the Rochester Meeting, American Chemical Society, September, 1913.

taken of the fermentative action of the microorganisms upon carbohydrates. In this class or group of media those in which lactose is used in combination with some nitrogenous substance are more often employed than any other. The diagnostic features upon which marked emphasis has been laid are: The total volume of gas produced; the rate of gas formation; and the composition of the gas, especially the volume proportion of CO_2 to gases not absorbed by alkalies; this latter proportionality has been termed the gas ratio. The total volumes of gas formed and the gas ratios obtained by different investigators, when working with the same bacterial species as described in the literature, agree fairly well, yet the variations are of sufficient magnitude to be beyond the limits of personal error. A careful search through the literature failed to show any systematic studies of the effects of the concentration of the different components upon the gases formed or of their effects upon the gas ratios. It appeared, therefore, that some interesting facts might follow the application of the methods described in the first paper of this series¹—that is to say, a study, by means of the triangular diagram as a guide, of the concentration of nitrogenous material, of inorganic salts, of acidity, and of carbohydrates in the media. It is obvious that such media are in reality four-component instead of three-component systems; but for the purposes of the investigation it was thought possible to hold one component at a time constant, and vary the other three. The method employed has been described at length and in detail in the first paper and need not here be discussed.

Since the most important of the fermentative bacteria, from the viewpoint of the water analyst, are those of the *B. coli* group derived from the feces of man and animals, our studies were confined to this group. In the greater part of the work we employed an artificial "sewage" thus prepared: One loopful of fresh moist feces (approximately 0.02 g.) was thoroughly shaken with 100 cc. of sterile water, filtered through sterile muslin into a sterile one-liter measuring flask and diluted to the mark with water from the University water supply pipes. This polluted water gave at different times from 2000 to 5000 colonies on standard gelatin at 20° at the end of forty-eight hours' incubation; approximately 200 colonies on agar at 38°, of which from 20 to 40 colonies proved to be assignable to the *B. coli* group.

In addition to this source of fecal bacteria, various polluted waters were tried, normal sewage, waters polluted with the feces of various domestic animals; and in addition fermentation tubes were inoculated with strains of pure cultures isolated from various sources.

Preliminary to the main investigation it was essential to determine whether under the conditions which would obtain in the preparation and

¹ THIS JOURNAL, 37, 1606 (1915).

sterilization of the culture media any marked inversion of the lactose would occur. With this end in view a large number of determinations were made upon culture media before and after sterilization, both in streaming steam in an Arnold sterilizer and also under pressure in an Adnet autoclave at 110° and 120° during periods of from 15 to 30 minutes. No change in the lactose could be detected with the low acidities employed, either by a sensitive Schmidt and Haensch polarimeter, or by gravimetric determinations of lactose by the Allihn or by the Deferen-O'Sullivan methods.

When the media were prepared from lactose, neutral inorganic salt and Witte peptone alone, with the reaction unadjusted, (*i. e.*, having a final acidity of from 1 to 1.2% due to the peptone), no perceptible change in acidity was detected after sterilization, care of course being taken to make all titrations at the same temperatures,¹ but with meat and liver broths marked changes in acidity always resulted during sterilization and upon subsequent standing.

In the course of the investigation, distilled water, water obtained by redistilling the laboratory-distilled water from acid permanganate, and water from the taps of the University water supply were in turn employed. Since the last source gave us somewhat more sensitive media it was employed in practically all the work hereinafter described.

The first series of experimental runs, using the triangular diagram as a guide, were undertaken with peptone, lactose and potassium chloride or sodium chloride as variables, the acidity being maintained constant in all the series at a value equivalent to 1% *N* HCl. The most rapid and most uniform fermentation was obtained in those media containing from 3 to 3.5% peptone, 0.6 to 1% lactose and 0.5 to 1.5% KCl or 0.5 to 1% NaCl, KCl being decidedly preferable.

Effect of Variations in Initial Acidity.—It having been ascertained, as stated below, that the lactose should be present in a medium in a concentration lying between 0.6% and 1%, it became possible by adopting a mean of 0.8% lactose in all media, to study, by means of the triangular diagram, the effect of the initial acidity. Runs, therefore, were made with concentrations plotted clock-wise upon the diagram as follows: Peptone, 1 to 6%; acidity, 0 to 2.5%; potassium chloride, 0 to 2.5%; lactose, 0.8%. In all the experiments tried, numbering several hundred, the most rapid gas formation and hence the first appearance of gas took place in media having an initial acidity of between 0.5% and 1.5%, expressed in cubic centimeters of *N* HCl with phenolphthalein as indicator. Other diagrams were now studied with peptone concentrations

¹ With the media as prepared in our laboratory a 3% peptone solution has a reaction of approximately +1% at 20° , +1.1% at 37° , and +1.5% at boiling (approximately 98°).

varying from 2 to 4%; potassium chloride, 0 to 1%; acidities, 0 to 10%. As before, gas appeared first and reached its maximum most rapidly in acid media. Neutral media yielded the greatest gas volumes,¹ but the gas was slower in appearing and showed greater variations in the final gas volumes than was the case of media having an acid reaction. An acidity equivalent to 1.5% appeared to be the upper limit of usefulness of media for diagnostic purposes. With low acidities media containing

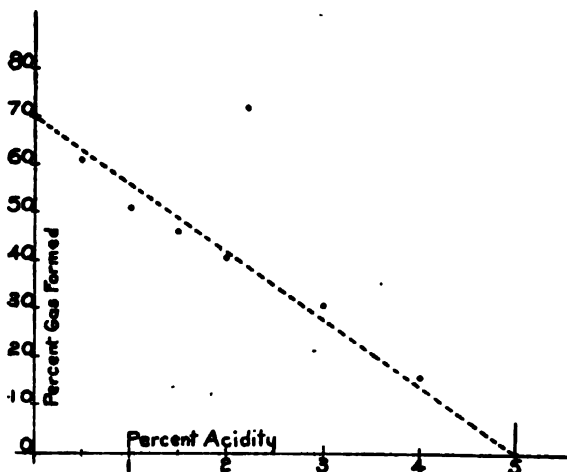


Fig. 1.

3, 3.5 and 4% peptone yielded gas volumes equivalent to over 50% of the closed arm of the fermentation tubes. The effect of initial acidity upon the total gas volume of a 3% peptone medium is shown graphically in Fig. 1, in which the average results obtained from a very large number of runs have been plotted. Proportionally similar results were obtained with higher peptone concen-

trations. In all the experiments made the addition of potassium chloride appeared to be distinctly beneficial.

Effect of Lactose Concentrations.—Since the reading of this paper W. W. Browne² has published the results of his investigation upon acid formation which has led him to reach the conclusion that 1% carbohydrate in a medium is sufficient for the maximum production of acid by members of the *B. coli* group. This is in agreement with the results obtained by us on gas formation. Stamm³ has found that from 0.5 to 3% of dextrose made little appreciable difference either in the total gas formed or in the gas ratio.

We tried systematically various media containing from 0.1% to 10% lactose. The results obtained confirmed those of Stamm with dextrose. Above 0.4% lactose up to 3% no appreciable effects upon gas volumes or upon rapidity of fermentation could be noted. Under 0.4% the gas volumes obtained were not uniform and the total gas formed occupied a

¹ W. W. Browne has found similar results as to total acidity produced. Neutral and slightly alkaline media yield a greater final acidity than media, having an initial acid reaction. See "Acid Production by *B. coli* Group," *J. Infect. Dis.*, 15, 580 (1914).

² Browne, *Ibid.*, *Loc. cit.*

³ Stamm, *Centr. Bakt. Parasitenk.*, 42, 590 (1906).

less volume of the closed arm than when lactose was present in higher concentrations. When 3% was reached a retardation in the rate of gas formation was noted and above this value the inhibiting effect was quite marked. For diagnostic purposes in water and sewage examinations the optimum conditions as to rapidity, large total volume of gas, and uniformity of results, appeared to lie between 0.6% and 1% lactose.

It was thought desirable to ascertain approximately the quantity of lactose fermented by the mixed flora of sewage in the diagnostic tubes. With this end in view, portions of lactose-peptone media were precipitated by phosphotungstic acid, filtered and the carbohydrate present in the filtrate determined by both the Deferen-O'Sullivan gravimetric method and by means of the polarimeter. Other portions of the same media were placed in fermentation tubes, inoculated with sewage, incubated at 37 to 38°, and as soon as no further gas increase could be detected the unchanged carbohydrate was determined in the media in the same manner as before. In the case of the inoculated and incubated samples the polarimeter gave slightly lower values for the lactose fermented than did the gravimetric method, doubtless due to the formation of optically active compounds formed in the fermentation of the lactose or in the decomposition of the peptone. It was found that from 25 to 35% of the lactose in 1% lactose media was all that the bacteria had converted into gas and other products. In other words, lactose media in practical work must contain approximately 0.6% lactose while any greater concentration than 1% is useless and uneconomical.

Effect of the Presence of Inorganic Salts.—The influence of the presence of NaCl and KCl in carbohydrate media in stimulating a more rapid fermentation by sewage organisms and assuring a greater uniformity in the total gas volumes formed has already been alluded to above. The methods employed in the study of the influence of the different inorganic salts available have also been described in our first paper.

As a result of our experiments upon lactose media with a mixed sewage flora and with pure cultures of members of the *B. coli* group, it is possible to arrange the inorganic salts tried into two groups:

I. Salts hastening fermentation and usually conferring greater uniformity of gas production.

KCl in concentrations up to 3.0%
K₂SO₄ in concentrations up to 3.0%
NaCl in concentrations up to 1.5%
Na₂SO₄ in concentrations up to 2.0%
MgSO₄ in concentrations up to 2.0%
CaCl₂ in concentrations up to 1 %

II. Salts having little influence upon gas production or acting as inhibiting agents.

KNO₃, NaNO₃, NH₄NO₃, NH₄Cl, (NH₄)₂SO₄; MgCl₂; MnCl₂; MnSO₄.

In Group I when the maximum concentration stated is approached an inhibiting effect is noticeable and if concentrations above these values are employed both the rate of fermentation and the final gas volume are reduced.

Potassium chloride having yielded the most satisfactory results, special runs were made with lactose at 0.8%; acidity, 1%; peptone, 3, 3.5 and 4% and with the KCl, 0 to 4%; each concentration differing from the next by 0.25%. Checks were also made, using NaCl. The results may be summarized as follows: (1) The addition of KCl lessened the time required for the first appearance of gas by from three to ten hours. (2) The total gas formed upon completion of fermentation was much more uniform in the different fermentation tubes containing media of like concentrations when KCl was present than where absent. (3) KCl appeared to be preferable to NaCl for rapid diagnostic purposes. (4) The best results were obtained with media containing from 0.5 to 1.5% KCl. (5) The total gas formed varied with the per cent. of peptone present but a 3%

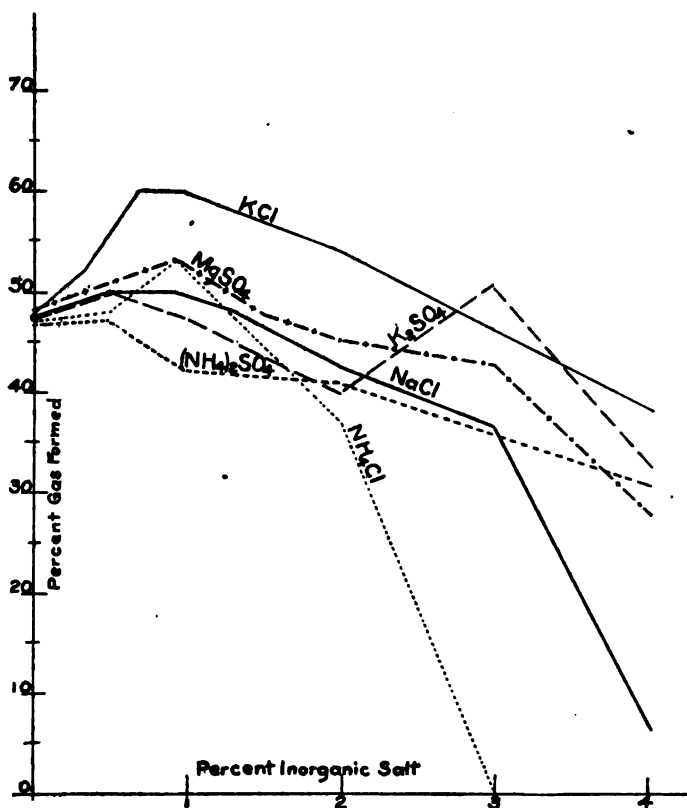


Fig. 2.

peptone from the viewpoint of rapidity and accuracy of diagnosis appeared to be as satisfactory as higher concentrations.

The average results of several hundred series of experiments using 3% peptone media and six typical inorganic salts are shown graphically in Fig. 2. It will be seen that in all cases a slight addition of an inorganic salt appears to stimulate fermentation.

The addition of salts of phosphoric acid to lactose-peptone media gave either no appreciable effects in very low concentrations or decidedly inhibiting effects in high concentrations.

The following phosphates were tested in different concentrations: Na_2HPO_4 , NaH_2PO_4 , NaKHPO_4 , $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, K_2HPO_4 , KH_2PO_4 , MgHPO_4 , NH_4MgPO_4 , CaHPO_4 . The concentrations of these phosphates which could be added without causing very voluminous precipitates during sterilization were found to be very low; usually as little as 0.02% produced a muddy unsatisfactory medium. In no case could we introduce a phosphate in concentrations above 1%. The salts KH_2PO_4 , K_2HPO_4 , MgHPO_4 , and NH_4MgPO_4 appeared to exert a slightly stimulating action upon gas production but in all the experiments tried the final gas volumes lacked uniformity save in the case of NH_4MgPO_4 alone. The last-named salt gave us better results than any other phosphate tried, but not so good as with media containing NaCl or KCl .

It may, therefore, be safely concluded that the amount of PO_4 ions present in peptone-containing media as ordinarily prepared is sufficient to meet the needs of a mixed sewage flora. Even so-called C. P. lactose usually contains phosphates; that employed in this investigation was found to contain 0.01% PO_4 . When a natural water instead of distilled water is employed a still further addition of PO_4 almost invariably results.

Effect of Peptone Concentrations upon Gas Volumes.—When the concentrations of inorganic salts do not exceed 1% and the acidity is maintained at between 1% and 1.5%, the total gas volume formed is proportional to the concentration of the peptone, meat, liver, or beef extract added until a point is reached where the viscosity is so great, or the concentration of certain materials present in these substances is so high, as to seriously interfere with the development of the mixed flora found in sewage.

In the results averaged in the curves shown in Fig. 3,¹ from some 3000 experimental inoculations, the lactose was kept constant at 0.8%, the acidity at 1%, the inorganic salt, in this case KCl , at 0.6%. The peptone was varied between 1 and 10%. Under these conditions there is a very

¹ In Fig. 3 the gas volumes indicated by the black dots are averages of results obtained with fermentation tubes of about 300 cc. closed arm capacity, used in the study of the composition of the gases of fermentation. The small circles are the averages of gas volumes obtained with ordinary fermentation tubes.

rapid rise in the total gas formed until a concentration of about 4% is reached, after which the increase in volume is slow and becomes approxi-

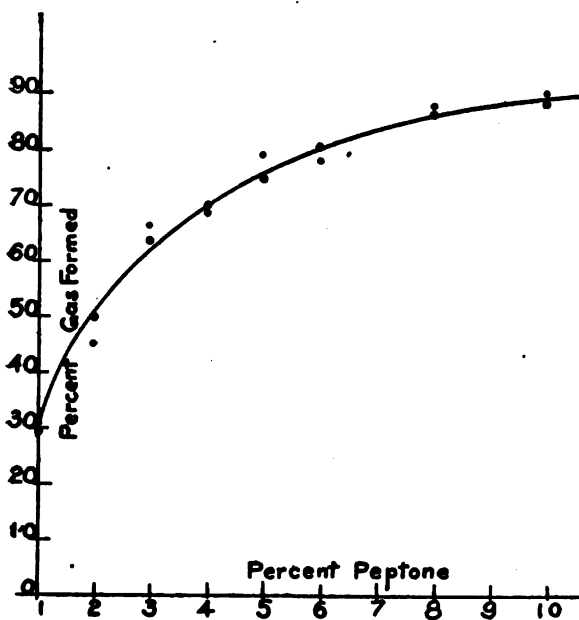


Fig. 3.

mately constant at a little over 10% peptone. Above 5% however, the rate of fermentation is materially reduced and with these high concentrations the fermentative process, in some cases, may not be completed for several days. The most rapid evolution of gas and completion of the fermentative process was always observed with concentrations of between 3 and 4% peptone.

In the opinion of the authors these results are the most interesting and important of the entire investigation. For it is obvious that a very slight variation in the proportion of peptone in low concentrations will result in a relatively great variation in gas volumes. Since peptone is very hygroscopic and since in the preparation of culture media it is the usual practice to exercise little care in weighing out this component, it follows that the media made at different times are apt to vary considerably in the nitrogenous component. A marked variation in the volume of gas formed will therefore result.

Water analysts have always believed that if great care is exercised in adjusting the acidity, this is sufficient to standardize the media. It appears, however, that for diagnostic purposes it is essential to use greater care in the proportioning of other components and that in reality a slight error in acidity between the limits commonly employed will effect the results much less than a variation in the concentration of the nitrogenous components, a fact which appears to have escaped attention.

Nor does this phenomenon apply to peptone alone for we have obtained similar increases in gas volumes with an increase in the proportion of beef flesh or beef liver. The results of these runs are shown in Fig. 4. In media prepared with beef or with beef or calves' liver, lactose was added in the

proportion of 0.8%, the reaction adjusted to +1% and in most of the runs 0.6% of KCl was added. When both peptone and meat or liver were used the change in gas volume in proportion to the concentrations was even more marked than in unpeptonized media. Since it may be

said to be practically impossible to purchase at a butcher shop meat twice alike as to composition, that is, as to proportion of flesh, fat, connective tissue, moisture, etc., it follows that we must expect at different times a variation of at least 10% in the final gas volumes unless we employ higher concentrations than is the rule. Moreover, we will show in our next paper that the composition of the gases of fermentation vary with the concentration of the nitrogenous components and therefore that the "gas ratio" obtained will depend upon the character of the medium employed.

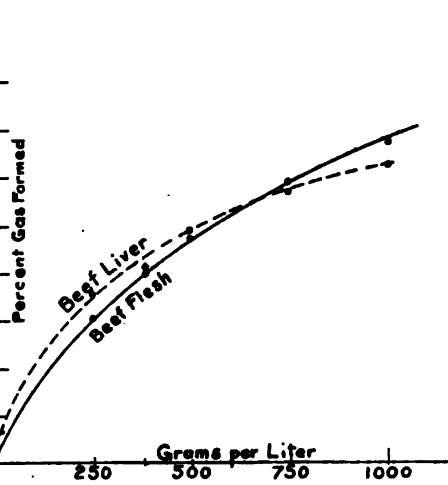


Fig. 4.

Media made with commercial "extract of beef" alone also yield larger gas volumes in higher concentrations. But in our hands the results have been exceedingly variable, and the total gas volumes usually small and, therefore, of no diagnostic values. Media containing high concentrations ferment very slowly; this is not surprising since their phosphate content is excessively high, so high in fact that large amounts of NH_4MgPO_4 invariably separate during the adjustment of the reaction and subsequently in the fermentation tubes; furthermore, the acidity of this material is so high that upon neutralization to, a reaction equivalent to +1% of N HCl a large addition of inorganic salt is made to that already present. Media made from commercial extract of beef, therefore, are apt to contain too high a concentration of inorganic salts other than phosphates and too low a concentration of the sort of nitrogenous matter necessary for the growth of fermentative bacteria. The fermentative process is therefore partially inhibited and the gas formed variable in volume and in composition.

Influence of the Size of Fermentation Tubes upon Gas Volumes.—

The total volume of gas which collects in the closed arm of the fermentation tube is by custom recorded and spoken of in terms of the length of this closed arm occupied by the gas. For convenience it is commonly expressed in per cent. This volume per cent. has been regarded as constant,

within narrow limits, for a given bacterial species and therefore is believed to be of considerable diagnostic value. We have pointed out above that the final gas volume is proportional to the per cent. of available nitrogenous material present in the medium. It remained to ascertain whether this held good for different styles of fermentation tubes. Excessively long (25 cm.) and excessively short (5 cm.) tubes were employed; tubes with diameters ranging from 4 mm. to 60 mm.; tubes containing 5 cc. up to 500 cc.; but in all cases we found that the gas volumes expressed in per cent. of the closed arms were substantially constant for a given peptone or meat concentration and that this per cent. appeared to be independent of the size of the closed arm of the tube, when the tube is of uniform diameter.

Composition of the Gases Formed.—Since the volume of the gas formed increases up to a certain maximum with an increase in the concentration of the peptone, meat, liver or meat extract present, and since the ratio of gases absorbed by KOH to those unabsorbed is employed in diagnosis, it became imperative to make careful analyses of the gases formed. The results obtained will be discussed in the third paper of this series. It will there be shown that the per cent. of CO₂ in the gas produced by sewage bacteria increases and the hydrogen decreases with the concentration of the nitrogenous material until a certain concentration is reached when the CO₂ and H no longer change.

Summary.

1. In the fermentation of lactose by bacteria in water contaminated by sewage, human feces, the feces of domestic animals, and pure strains of the *B. coli* group, the total volume of gas formed increases to a final maximum with the concentration of the peptone, meat, liver, or meat extract employed.

2. The composition of the gas formed is dependent upon the concentration of the nitrogen-containing substance employed.

3. The addition of from 0.5 to 1% of KCl to lactose-peptone media appears to stimulate fermentation and assure more uniform results.

4. Similar beneficial effects are obtainable with NaCl, but of not so marked a character.

5. Nothing is to be gained by employing a lactose concentration of over 1%.

6. Neutral media appear to yield slightly greater gas volumes than media slightly acid to phenolphthalein; but media having a reaction of approximately +1% ferment considerably more rapidly and yield diagnostic results in several hours' shorter time.

7. The gas ratios of organisms of the *B. coli* group are dependent upon the concentration of the peptone or other similar nitrogenous material in the media.

8. The addition of meat infusion to peptone media improves this media

when low concentrations of peptone are employed, but yields media whose reactions rapidly change.

9. A very sensitive peptone culture medium yielding uniform results and large gas volumes consists of peptone 3 to 4%, lactose 0.8%, potassium chloride 0.6%, reaction +1%. Such media show little change on keeping.

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[CONTRIBUTION FROM THE ROBERT HARE LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.]

THE DISTRIBUTION OF ARSENIC IN LIVER TISSUE IN CASES OF POISONING.

By LEON A. RYAN.

Received June 14, 1915.

This investigation was undertaken to ascertain if arsenic administered to an animal, either in its food or by subcutaneous injections, is equally distributed in the liver tissue of the animal. From the nature and structure of the liver it would most naturally be expected that the arsenic would be uniformly distributed throughout this organ.

Dog No. I.—A male dog, weighing 18 pounds, in which a permanent biliary fistula had been established and the common duct ligated with another object in view, received subcutaneous injections in the neck, shoulders, abdomen and legs of various volumes of a solution of sodium arsenite equivalent to 0.001 mg. of arsenious oxide per cubic centimeter. The total amount of sodium arsenite solution injected in different parts of the body during seven successive days was equivalent to 191.5 mg. of arsenious oxide. Death of the dog occurred on the eighth day.

Immediately after the death of the dog an autopsy was made. The liver appeared of normal size for a dog weighing 18 lbs. No abnormal coloring of the liver substance was observed. The weight of the liver immediately after removal was 338.7 g.

The liver tissue in the case of each dog was decomposed by the Fresenius-von Babo method.

Dog No. 1.				
Part of liver analyzed.	Moist wt. in grams.	Gram As_2S_3 obtained.	Equiv. to As_2O_3 .	Per cent. As_2O_3 in moist tissue.
Left lateral lobe.....	80.6	0.0018	0.0014	0.0017
Left central lobe	115.78	0.0023	0.0018	0.0015
Right central lobe				
Caudate lobe	121.39	0.0027	0.00217	0.00178
Right lateral lobe				

Dog No. II.—A solution of sodium arsenite containing progressively increasing quantities of the compound was mixed with cracker crumbs and, with other food, fed to a dog weighing 24 pounds. The administra-

tion covered a period of 19 days when the dog died. The amount administered aggregated the equivalent of 1.025 g. As_2O_3 .

The liver removed from the dog on the nineteenth day weighed 350 g.

Dog No. II.				
Part of liver analyzed.	Moist wt. in grama.	Gram As_2S_3 obtained.	Equiv. to As_2O_3 .	Per cent. As_2O_3 in moist tissue.
Left lateral lobe.....	113.94	0.0022	0.00176	0.00155
Left central lobe	114.20	0.0021	0.00165	0.00144
Right central lobe				
Caudate lobe	131.82	0.0022	0.00176	0.00134
Right lateral lobe				

Conclusion.

The foregoing results show that the arsenic of soluble arsenical compounds administered either subcutaneously or by the mouth to dogs until death occurs is uniformly distributed throughout the tissue of the liver.

PHILADELPHIA, PA.

NOTE.

Note on Goeldner's Test for Cocaine.—In a brief note published in the *Pharmaceutische Zeitschrift für Russland*, 28, 489, and copied verbatim in the *Zeitschrift für Analytische Chemie*, 40, 820 (1901), M. Goeldner describes a qualitative test for cocaine which is as follows: Mix about 0.01 g. of pure resorcinol in a small dish with 6 or 7 drops of pure, concentrated sulfuric acid. Add about 0.02 g. of cocaine hydrochloride to this solution which usually has a faint yellowish color. There is a vigorous reaction, during which the liquid acquires a beautiful blue color like that of the corn flower. The intensity of this color gradually increases. Sodium hydroxide solution changes the blue color to light pink.

On applying this test with chemically pure materials, it was found that no response as described by M. Goeldner could be obtained. This led to an examination of the conditions pertaining to the test with the following results: When the required amount of chemically pure resorcinol, 0.01 g., was mixed with 6 or 7 drops of chemically pure concentrated sulfuric acid, a faint yellowish color was obtained but when the specified amount of cocaine hydrochloride (0.02 g.) was added the "beautiful blue color like that of corn flower" failed to develop. If, however, concentrated sulfuric acid containing minute traces of nitrates or nitrites was brought in contact with resorcinol alone, a beautiful blue color was produced. The coloration obtained by M. Goeldner was, therefore, due to a trace of nitrous or nitric acid in the sulfuric acid employed and not to the presence of cocaine. This is in accord with the observation¹ that if resorcinol be heated with sodium nitrite, it forms a deep blue dye, soluble in water which,

¹ *Ber.*, 17, 2617 (1884).

according to a later observation,¹ is composed of two dyes—resorufin and resazurin, derivatives of phenoxazine.

By further experimentation it was found that 1 cc. of a potassium nitrate solution containing 0.0000001 g. of nitrogen as potassium nitrate, when carefully evaporated to dryness, and the residue moistened with chemically pure sulfuric acid, yielded a blue coloration when a small amount of solid resorcinol was added. The extreme delicacy of this test would, therefore, render it valuable to detect minute traces of nitrates and nitrites in residues obtained in the course of a water analysis.

LEON A. RYAN.

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NEW BOOKS.

Molecular Association. By W. E. S. TURNER. Pp. viii + 170, with diagrams. (Monographs on Inorganic and Physical Chemistry, edited by A. Findlay.) Longmans, Green & Co., 1915. Price, \$1.40 net.

There appears to be a fairly wide-spread impression that molecular association is a phenomenon which occurs relatively infrequently; but this view is erroneous, for further investigation of the matter always extends the list of associated substances, so that it would seem that some degree of association is of very general occurrence. Nor is it generally realized that the degree of association is not a fixed quantity but varies with a number of factors, of which the most important are temperature, pressure, electrical stress and solvent action; so that it is plausible that by a suitable choice of conditions one could obtain any substance partly associated just as one may obtain almost any solid substance in colloidal form. The author brings together the relevant experimental evidence—which, it may be remarked, leaves much to be desired as regards both quality and extent—and exhibits the present status of the question; the discussion will bring before the reader the present plentiful lack of definite information on this important topic. There is a list of 275 references to the text and an appendix, covering more than forty closely printed pages, in which the experimental data on the molecular complexity of dissolved substances are tabulated and summarized; these features alone render the book a desirable addition to the library.

JOHN JOHNSTON.

Einführung in die Metallographie und Wärmebehandlung. VON DR. ING. H. HANEMANN, Dozent für Metallographie und Materialkunde an der Königlichen Technischen Hochschule zu Berlin. Berlin: Gebrüder Borntraeger. 1915. vii + 128 pp. Price, 8.50 M.

This book is made up of twelve lectures delivered in a summer course

¹ Ber., 23, 718 (1890).

in the Technical High School of Berlin. The subject matter deals with the fundamental laws of crystallization as applied to metals, the establishment and significance of equilibrium diagrams of binary and ternary alloys, and discussion of special cases of some technically important binary systems and especially of the iron-carbon system. The phenomena of hardening, tempering and annealing of steels, while condensed, are logically and clearly treated, and the reader should obtain a clear idea of the physics of heat treatment, and its relationship to changes in physical properties. Etching of steels for macroscopic and microscopic observation and the interpretation is discussed, and a series of excellent microphotographs appended illustrate the text. Special steels are mentioned briefly.

For those who wish to know something of the principles of the metallography of iron and steel, but do not care for a detailed study, the book is excellent.

HENRY FAY.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS. II.

By I. M. DENNIS AND P. A. VAN DER MEULEN.

Received July 2, 1915.

In a recent number of *THIS JOURNAL*¹ there was described a method for the fractional separation of the rare earths by means of the electrolysis of neutral solutions of their nitrates. The present article describes results that were obtained in a further study of that method.

Dennis and Lemon electrolyzed a solution of the nitrates of various rare earths, using a cathode of mercury and an anode of platinum. They did not employ a diaphragm, and consequently it was possible that the separation of the rare earths they obtained might be ascribed to the fractional precipitation of the hydroxides of the earths by the ammonia formed by cathodic reduction of the nitric acid. To ascertain whether the rare earths could fractionally be separated by the electrolysis of solutions of their salts under such conditions as would preclude the formation of ammonia, a solution of the chlorides of the earths was subjected to electrolysis.

I. Electrolysis of a Neutral Solution of the Chlorides of the Rare Earths.

Material.—The material that was employed for this electrolysis consisted of about 1200 g. of the oxides of the yttrium group from which the

¹ Dennis and Lemon, *THIS JOURNAL*, 37, 131 (1915).

cerium had been separated by chlorination, and almost all of the didymium earths had been removed by precipitation with sodium sulfate. The purified material contained neither iron nor other common elements, and its solution showed no absorption bands of neodymium.

A neutral solution of the chlorides of these earths was prepared by slowly adding the oxides to warm dilute hydrochloric acid until the oxides were in slight excess. The liquid was then heated to boiling in the presence of the excess of oxides until a test with Congo-red paper showed that all of the acid had been neutralized. The undissolved oxides were then removed by filtration, and the filtrate was diluted with distilled water until it contained an amount of the chlorides equivalent to 10% by weight of the solution in oxides of the rare earths.

Apparatus.—The cell that was used for the electrolysis was a thick-walled glass cylinder with an internal diameter of 32.5 cm. and a depth of 35 cm. A layer of mercury 1.5 cm. deep was placed in the bottom of this cylinder, a glass cup filled with mercury was set in the middle of the bottom of the cylinder, and a porous cup 5 cm. in diameter and 12 cm. high was placed upon this glass cup base. Electrical connection with the layer of mercury was made by fusing a short platinum rod through the end of a glass tube, filling the tube with mercury, and then fastening this tube in such position in a clamp that the projecting end of the platinum dipped into the mercury in the cylinder. A cylindrical carbon rod, 2 cm. in diameter and 30 cm. long, inserted in the porous cup served as anode. The chlorine gas that was liberated at the anode was carried off to the flue by fitting the top of the porous cup with a perforated rubber stopper, and blowing a current of air through the cup. The neutral solution of the chlorides of the rare earths was poured into the cell upon the layer of mercury, and this solution and the mercury were vigorously stirred throughout the electrolysis by air that was blown through three glass tubes that dipped below the surface of the mercury. Current for the electrolysis was taken from a 110 volt direct circuit through a lamp bank. An ammeter was connected in series with a cell and a voltmeter was connected across the terminals.

Procedure.—After the cell had been charged in the manner above described, the porous cup was placed upon its support in the middle of the cell, and was filled with dilute hydrochloric acid (0.1 *N*) until the level of the acid inside the cup was slightly below the surface of the solution in the cell. The carbon anode was then set in position within the cup, connections with the source of current were made, the air for stirring the mercury cathode was turned on, and the electrolysis was continued until the equivalent of about 40 g. of oxides of the earths had been precipitated at the cathode in the form of hydroxides.

— The character of the hydroxides obtained in this manner is entirely

different from that which results from the precipitation of a solution of the earths with an alkali hydroxide. The electrolytic precipitate is granular, and appears to possess a crystalline character, although a microscopic examination failed to show crystalline characteristics.

When the desired amount of the rare earths had been precipitated, the current was turned off, the agitation of the mercury cathode by air was discontinued, the precipitated hydroxides were allowed to settle, and the supernatant liquid was siphoned off. The precipitate and the mercury at the bottom of the cell were transferred to a separatory funnel, and the mercury was drawn off. The hydroxides were then thrown upon a Büchner funnel and were thoroughly washed with water. They were next warmed with dilute hydrochloric acid, which dissolves the hydroxides readily, but left most of the finely divided mercury undissolved. The undissolved mercury was separated by filtration, and the small amount of mercury that had passed into solution was removed by precipitation with hydrogen sulfide. The filtrate was freed from hydrogen sulfide by boiling, and the rare earths were then precipitated by oxalic acid. The oxalates were washed with hot water until free from chlorides, and were then dried. A small portion of this precipitate of the oxalates was set aside for the determination of the average atomic weight of the earths, and the remainder of the oxalates was converted to the oxides by heating in a platinum dish.

The supernatant liquid that was siphoned off from the hydroxides precipitated during the electrolysis, and the wash water from the washing of these hydroxides were united, placed in the cell, and the electrolysis was repeated until the second fractional precipitate of hydroxides of the earths was obtained. This precipitate was purified as before, and the procedure was repeated until nearly twenty fractions resulted. As the end of the fractional precipitation was approached, the voltage across the terminals of the cell rose because of the decreasing concentration of the electrolyte.

The atomic weight of each fraction was determined by the oxalate-oxide method. The absorption spectrum of each fraction was observed with a Krüss spectrocope in the manner described by Dennis and Bennett.¹ The solution employed for this purpose was prepared by dissolving 5 g. of the oxide in a slight excess of hydrochloric acid, removing the excess of acid by evaporation and diluting the solution to 25 cc. with distilled water. Whenever Congo-red paper showed there was still an excess of acid, the evaporation was repeated until the free acid was removed.

The details of this series of electrolyses are given in Table I. The atomic weights of the various fractions and the relative intensities of dis-

¹ THIS JOURNAL, 34, 7 (1912).

tinctive absorption bands of the different colored earths in the fractions are plotted in Plate I. The spacing of the fractions along the axis of abscissas is based upon the actual weights of the several fractions.

TABLE I.—ORIGINAL ATOMIC WEIGHT, 106.6.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	121.98	26	8.4	100	Oxalates pink, color deepened through No. 4, after which it faded. The oxalates of fractions 19 and 20 were almost white.
2	123.79	57	8.5	154	
3	122.12	42	8.4	114	
4	121.16	54	8.0	121	
5	115.55	36	8.0	87	The oxides were of a brownish yellow color which deepened to fraction 4 and then gradually became lighter.
6	113.37	55	8.2	150	
7	110.71	56	7.5	155	
8	108.69	46	9.2	143	
9	106.74	40	8.0	141	
10	104.28	44	8.5	129	
11	103.11	40	7.5	109	
12	97.09	30	8.0	97	
13	98.87	40	10.1	164	
14	99.03	38	9.0	132	
15	98.63	36	8.5	110	
16	98.27	25	10.0	170	
17	96.53	40	10.5	137	
18	96.12	55	10.9	152	
19	94.28	50	11.0	153	
20	93.16	41	13.0	179	

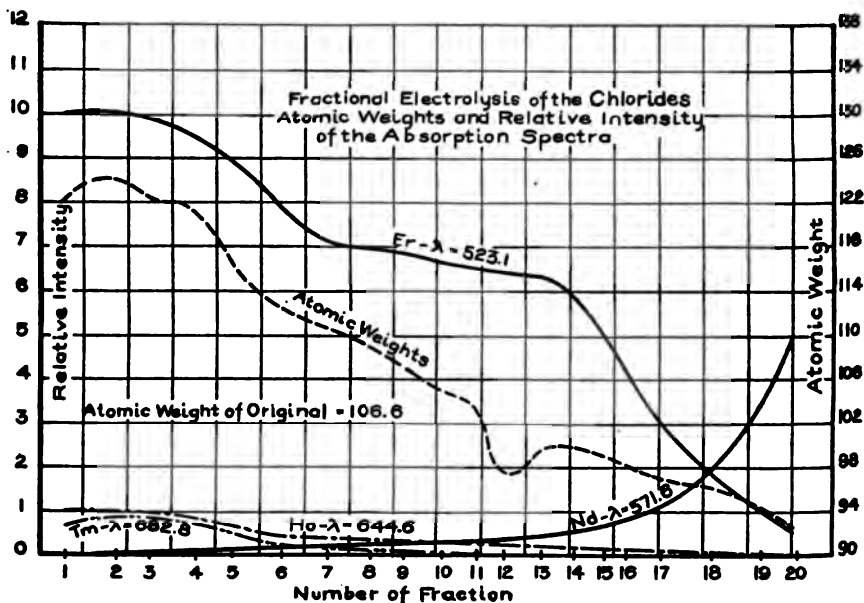


Plate I.

The results obtained in the above fractional electrolysis of a neutral solution of the chlorides of the rare earths demonstrate that the earths of the yttrium group can fractionally be separated under conditions that preclude the formation of ammonia or other basic precipitant. The absorption spectra of the fractions show that the colored earths, erbium, holmium and thulium, are concentrated in the early fractions. Neodymium, which was present in the original solution in such slight amount that its absorption bands were not discernible, was concentrated in the later fractions. The low atomic weights of the last four fractions show that yttrium is precipitated chiefly in the later fractions.

The voltage that was employed in the electrolysis of the chlorides was undoubtedly considerably higher than the decomposition voltage of the salts of the various rare earths that were present. The question naturally arose as to whether the decomposition voltages of the salts of the rare earths might be utilized in obtaining a sharper separation of the different earths than seemed to be possible with higher voltage. To obtain information upon this point, the following experiments were made.

II. Decomposition Voltages of Solutions of Salts of the Rare Earths.¹

The solution of the rare earth under examination was placed in a small U-tube of 9 cc. capacity, and 8 mm. internal diameter. Dipping into the solution in the two arms of this tube were two terminals of platinum wire. These were cleaned with care, and heated to redness before each determination. These terminals were connected through a galvanometer and switch to a slide wire-resistance, by means of which a gradual change of potential from zero to three volts could be obtained. This potential difference was accurately measured by means of a standard voltmeter that was sensitive to 0.002 volt. The current flowing through the cell was measured by the deflection of a galvanometer which was observed through a telescope. The resistance of the galvanometer was so small that the error caused by placing it in series with the cell was negligible. That such was the case is shown by the fact that when a potential difference so slight that it could not be read on the voltmeter was established between the terminals, with the cell cut out, the deflection of the galvanometer was beyond its highest scale reading.

The solutions of the rare earths that were employed in these measurements were prepared by precipitating the hydroxides of the earths with ammonium hydroxide, washing the precipitate on a Büchner funnel with hot water until it was free from ammonium salts, and then bringing the precipitated hydroxide into contact with an amount of the acid that was just insufficient to dissolve all of the precipitate. The solution was boiled for several minutes with the excess of the hydroxide to ensure

¹ Mr. A. B. Ray, who also is carrying on investigation in this field, collaborated in the determination of these decomposition voltages.

complete neutralization of the acid. The residual precipitate was then removed by filtration. The concentration of the solution was determined by analysis, and it was then diluted with water until it was of exactly normal strength.

In this manner normal solutions of the nitrates of thorium, lanthanum, cerium and neodymium and of the chlorides of thorium and cerium were prepared.

The decomposition voltage of one of these solutions was determined by placing the solution in a U-tube, making connections in the manner above described, and then gradually raising the potential difference across

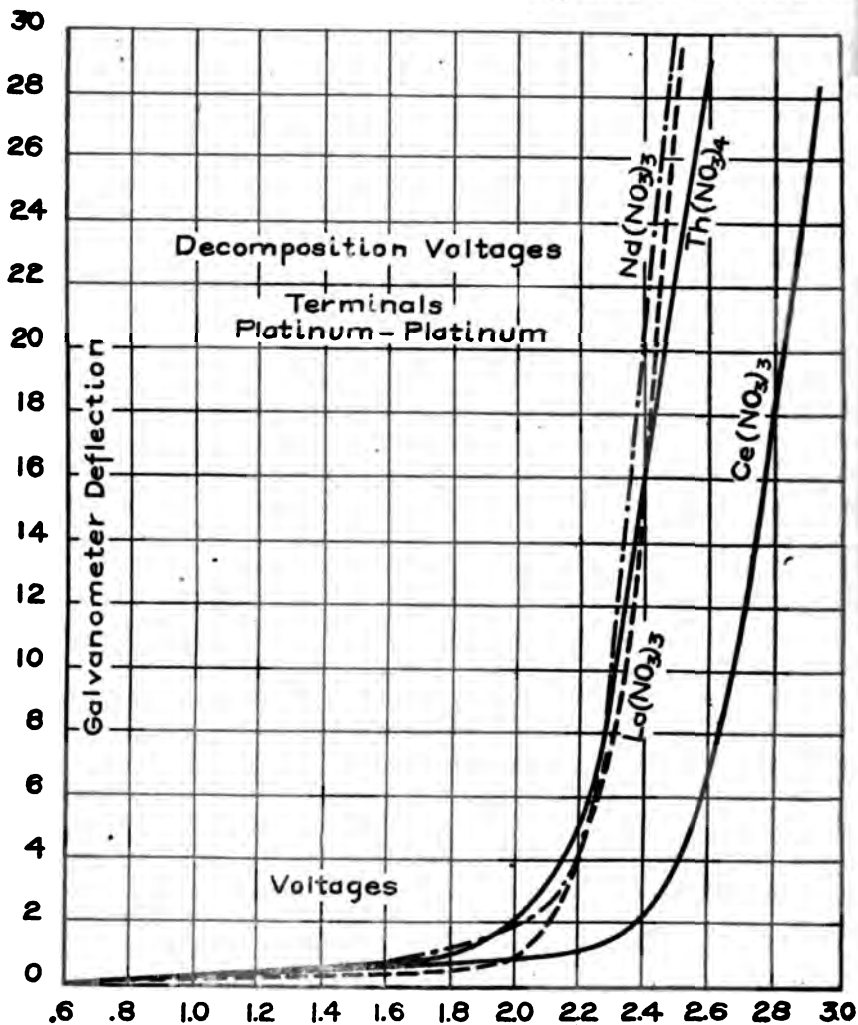


Plate II.

the cell by increasing the external resistance. With each change of potential, connection with the galvanometer was made by throwing in the switch, and the reading of the instrument was taken after the initial momentary deflection had subsided. As the decomposition value, which had to be located approximately beforehand, was approached, very small increments in potential were taken, which gave a large number of points in this region. From the readings thus obtained curves were plotted, using potential differences as abscissas and the galvanometer deflections as ordinates. The point at which the curve shows a decided break is the decomposition value. Sometimes the curve, after passing this point,

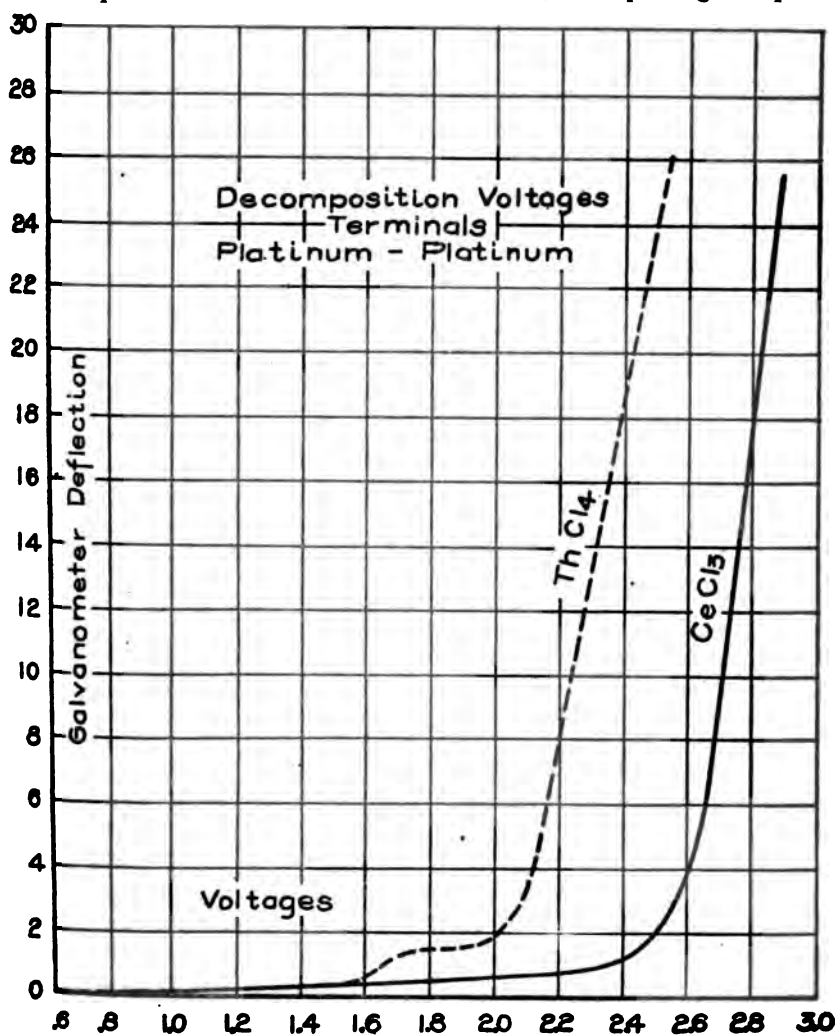


Plate III.

showed peculiar behavior in that it did not rise in a straight line. This was probably due to slight electrolytic decomposition and deposition at one or the other of the terminals. In every case, however, the break came at the same point.

The results that were obtained in the measurement of the decomposition voltages of neutral solutions of the nitrates of thorium, neodymium, lanthanum and cerium, using terminals of platinum, which are plotted in Plate II, were as follows:

TABLE II.

	Volts.		Volts.
Thorium nitrate.....	1.87	Lanthanum nitrate.....	2.05
Neodymium nitrate.....	2.03	Cerous nitrate.....	2.18

The decomposition voltages of neutral solutions of the chlorides of thorium and cerium with terminals of platinum are shown in Plate III, and were:

TABLE III.

	Volts.
Thorium chloride.....	1.94
Cerous chloride.....	2.36

It was further thought desirable to ascertain the decomposition values of some of these salts under conditions that simulated as closely as possible those pertaining in the fractional electrolysis with an agitated mercury cathode.

The container that was here employed consisted of a glass tube with a platinum wire sealed through the closed lower end and a side arm sealed to the tube a short distance above the lower end and bent upward. Mercury was poured into the larger tube until the level of the metal reached nearly to the opening of the side tube, and the main tube and side arm were then filled nearly to the top with the solution under examination. The mercury was kept in agitation by bubbling air through it, the air being passed in through a small tube inserted from above. A platinum wire extending down a short distance into the solution in the side arm served as anode. The results that were obtained with this apparatus are plotted in Plate IV, and were as follows:

TABLE IV.

	Volts.
Thorium nitrate.....	1.06
Cerous nitrate.....	1.10
Neodymium nitrate.....	1.24

These measurements show that the decomposition voltages of solutions of such salts of the rare earths as were here employed lie quite close together, and usually increase with the increase of the basicity of the earth. The decomposition voltages of the nitrates of thorium, neodymium and cerium, when a mercury cathode and platinum anode are employed, are considerably lower than the values obtained between platinum

terminals, but the differences are no more pronounced. From these results it is apparent that a sharp separation of the different earths one from another cannot easily be effected by adjustment of the voltage.

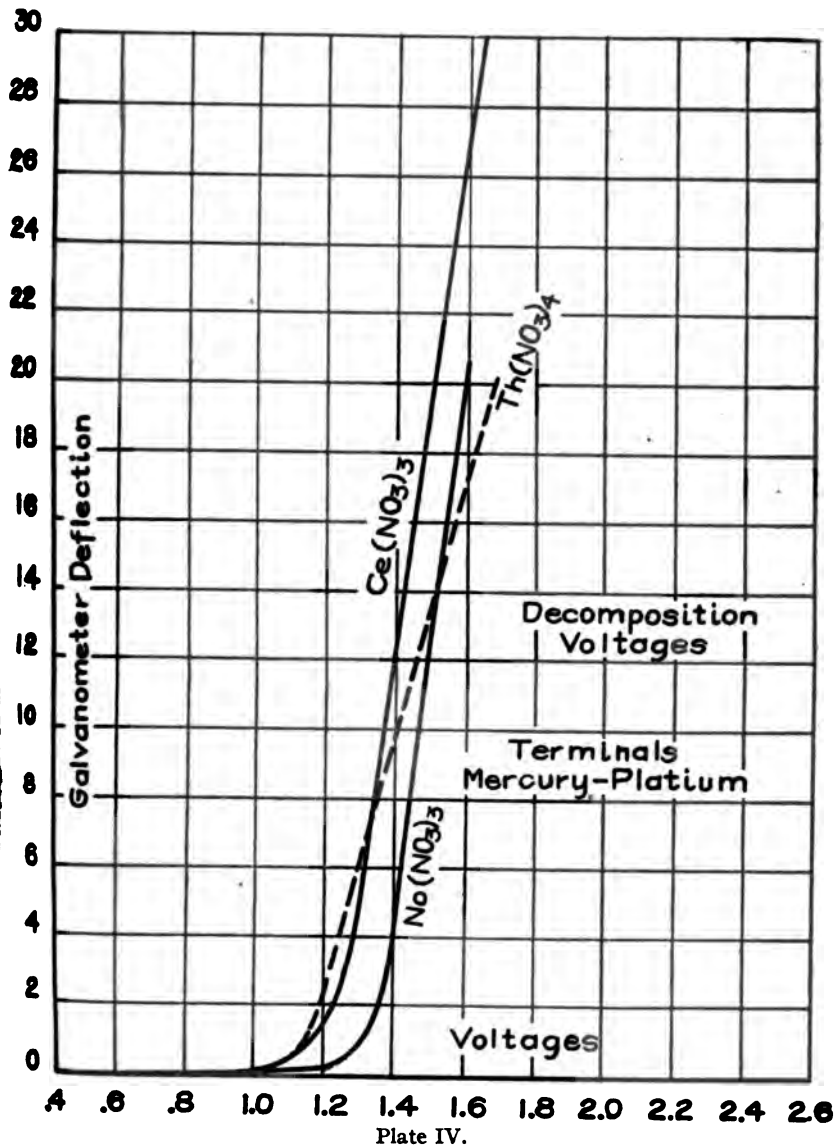


Plate IV.

Moreover, the precipitation of the hydroxides of the earths at these low voltages is so slow as to, of itself, preclude the utilization of these decomposition values in the rapid fractionation of comparatively large amounts of the rare earths. For these reasons recourse was again had to the frac-

tional electrolysis of solutions at voltages considerably above the decomposition values. Preliminary experiments having shown that no ammonia is formed when a solution of the nitrates of the earths is electrolyzed with a mercury cathode, and with a platinum anode that is placed in a porous cup, this modification of the procedure was next subjected to examination.

III. Electrolysis of a Neutral Solution of the Nitrates of the Rare Earths, Using a Diaphragm.

The oxides of the rare earths that were obtained in the twenty fractions of the electrolysis of the chlorides were united and were boiled with an amount of nitric acid that was not quite sufficient to dissolve them completely. The excess of oxides was removed by filtration and the neutral nitrate solution, which contained about 700 g. of the oxides, was diluted to 10 liters. This volume of the solution was maintained throughout the electrolysis. A sheet of platinum 5 cm. square was used as anode. In other respects the cell was exactly the same as that used in the electrolysis of the chlorides. The nitric acid that accumulated in the anode cup was removed by allowing distilled water to drop into the cup from a separatory funnel, and keeping the height of liquid in the cup constant by means of a siphon. A current of 5 amperes was used. The voltage varied from 7.5 to 18. The conduct of the electrolysis, the treatment of the fractions and the determination of the atomic weights of the fractions were performed in exactly the same manner as in the fractionation of the chlorides.

The fractional electrolysis of this solution of the nitrates, using a diaphragm, was found to precipitate the hydroxides of the earths about four times as rapidly as in the chloride electrolysis. It was possible that the hydrogen set free at the cathode might reduce some of the nitric acid to ammonia, as was found to be the case when no diaphragm was employed. Careful qualitative tests of the solution after the ninth fraction had been removed failed, however, to show the presence of a trace of ammonia. The results of this fractional electrolysis of the nitrates are shown in Plate V and Table V.

TABLE V.—ORIGINAL ATOMIC WEIGHT, 106.6.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere hours.	Remarks.
1	123.84	67	7.45	83.68	Color of oxalates was pink in first fraction, becoming gradually lighter; last three fractions were pure white.
2	120.85	75	6.90	83.9	
3	114.14	80	7.33	107.9	
4	108.08	85	7.25	100.7	
5	104.75	77	7.37	88.43	
6	101.65	92	8.00	99.9	Contained no cerium.
7	94.95	72	10.00	101.7	
8	98.94	60	12.75	75.68	Contained cerium.
9	91.63	40	18.00	62.27	Very slight trace of cerium.
10	94.43	16	Precipitated by oxalic acid		

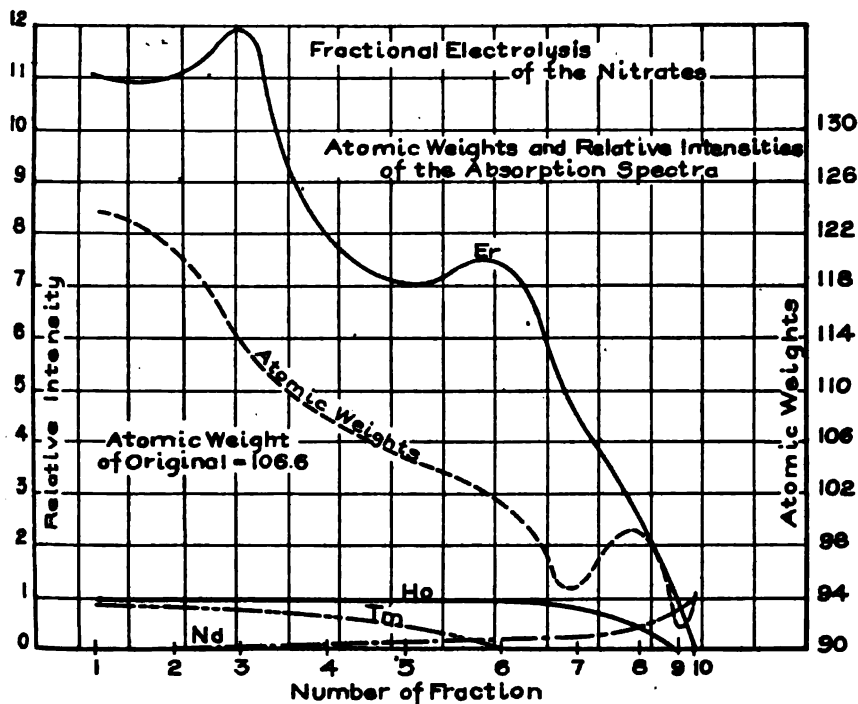


Plate V.

It will be noted that in this series of electrolyses the colored earths erbium, holmium, and thulium were present in preponderating amount in the first four fractions, and were probably accompanied by considerable amounts of yttrium, as is indicated by the relatively low average atomic weight of the earths in these fractions. The last fractions, however, consist chiefly of yttrium, mixed with small amounts of cerium and neodymium that also were concentrated at this point. The method yields, therefore, in the first fractions a rapid concentration of erbium that is nearly entirely free from the didymium group; and, in the later fractions, yttrium that is quite free from the colored earths of the erbium group, but is accompanied by any of the didymium group that may have been present in the original solution. It is interesting to note that the later fractions contained detectable amounts of cerium, although qualitative tests of the original solution failed there to disclose the presence of this element. To obtain further indication as to the efficiency of the method in the separation of the earths of the erbium and yttrium groups, the first four fractions given in Table V were combined, and were converted into a neutral solution of the nitrates. The weight of the oxides in the solution was about 220 g., the volume of the solution was 2300 cc., and the average atomic weight of the earths was 116.54. A cell measuring 21

cm. in diameter and 20 cm. in height was used for the electrolysis. In other respects the same apparatus was employed as before. Six fractions were obtained by electrolytic precipitation. The liquid remaining after the last fraction had been removed possessed high resistance and gave no precipitate with oxalic acid. The results of this fractional electrolysis are shown in Plate VI and Table VI. These results again demonstrate the efficiency of the method in speedily concentrating erbium and yttrium at opposite ends of the electrolytic fractionation, and in the concentration of the erbium earths practically free from the didymium group.

TABLE VI.—ORIGINAL ATOMIC WEIGHT, 116.54.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	137.2	30	6.7	37	Oxalates of first three fractions, were a deep pink, fading gradually.
2	129.04	48	6.2	45	
3	119.76	45	6.0	45	
4	111.61	38	6.9	47	Fraction 6 was nearly white.
5	99.58	35	11.0	42	
6	95.08	15	29.0	25	

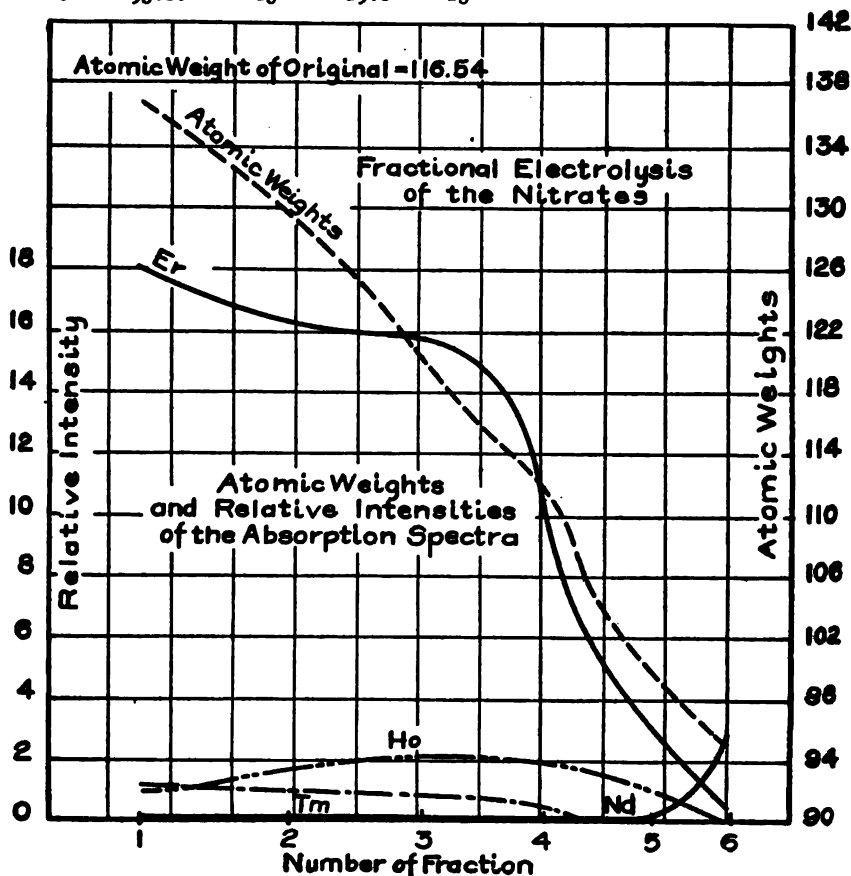


Plate VI.

The eighth fraction, Table V, Plate V, showed a sudden rise in atomic weight, which was probably due to the concentration of neodymium in the later fractions of that run. With a view to ascertaining whether the method of fractional electrolysis might profitably be utilized in separating neodymium (and its group elements) from the erbium group, even when the amount of material is comparatively small, the oxides constituting the eighth fraction were converted to a neutral nitrate solution that contained about 45 g. of rare earth oxides in 600 cc. of solution and this was fractionally electrolyzed in the same manner as before. Six fractions were obtained. The results given in Table VII and Plate VII again demonstrate the ease and rapidity of the separation of neodymium from yttrium and erbium.

TABLE VII.—ORIGINAL ATOMIC WEIGHT, 98.94.

Fraction No.	Atomic weight.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	97.67	8.0	6.8	9.6	The oxalates were pink,
2	97.11	9.5	8.2	9.6	fading rather rapidly.
3	94.36	8.5	8.0	9.6	The oxides were light
4	94.04	9.0	11.6	10.5	yellowish brown, and
5	93.24	6.0	19.0	8.4	about the same color.
6	104.27	3.0	Precipitated by oxalic acid		Very dark brown oxide.

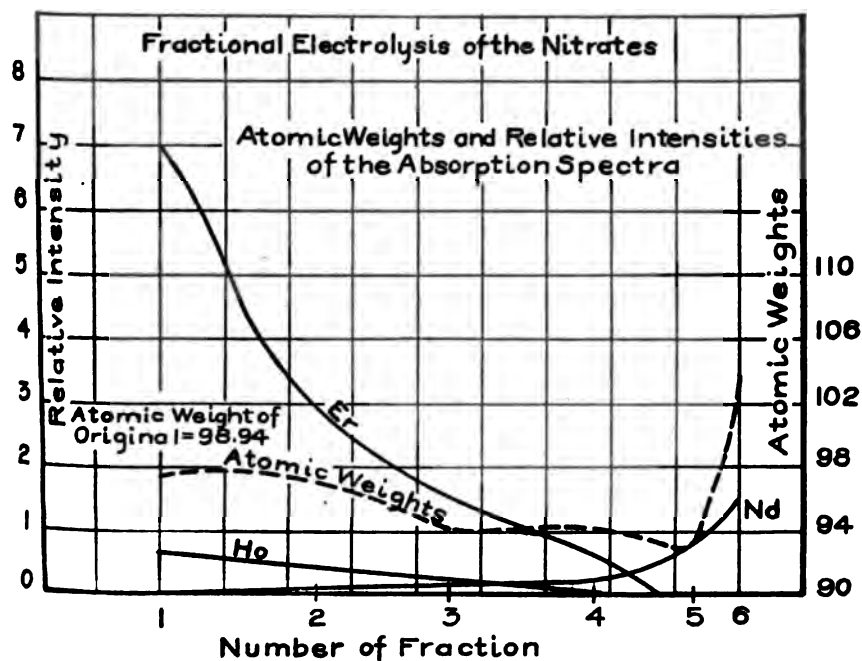


Plate VII.

The separation of the rare earths by the fractional precipitation of their hydroxides upon electrolysis of solutions of their salts at voltages considerably higher than the decomposition values of the salts is probably due to the action of the hydroxyl ions, concentrated near the cathode, upon earths of different basicities. The hydroxide of the weakest base will first tend to form, and if the deposition of this insoluble hydroxide upon the surface of the cathode be prevented, and if the electrolyte be rapidly stirred throughout the electrolysis, a progressive precipitation of the hydroxides of the earths, in the order of their basicities, will result.

Summary.

1. The decomposition voltages of several neutral, normal solutions of salts of the rare earths were determined. The values were found to lie close together and to be in the neighborhood of two volts.

2. Fractional electrolysis of a solution of the chlorides of the yttrium earths yielded rapid concentration of the colored earths in the earlier fractions, and of yttrium in the later fractions. A small amount of neodymium that was present appeared in the last fractions.

3. Fractional electrolysis, with a diaphragm, of a solution of the nitrates of these earths showed concentration of the earths similar to that obtained in the electrolysis of the chlorides. The rate of precipitation of the hydroxides of the rare earths from the nitrate solution was, however, four times as rapid as from the chloride solutions. No ammonium salts were present in the electrolyte at the close of the run.

4. Fractional electrolysis of a solution high in erbium, holmium, thulium and yttrium gave, in a series of six fractions, no appreciable separation of the first three earths one from another, but rapidly separated the three from yttrium.

5. In the fractional electrolysis of solutions of certain salts of the rare earths, the hydroxides of the earths are precipitated, under the conditions here described, in the order of the basicities of the earths. Rapid concentration of certain groups of earths is attained in short series of fractions.

The method is being further studied in this laboratory.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE EQUILIBRIUM BETWEEN CARBON OXYSULFIDE, CARBON MONOXIDE AND SULFUR.

BY GILBERT N. LEWIS AND WILLIAM N. LACEY.

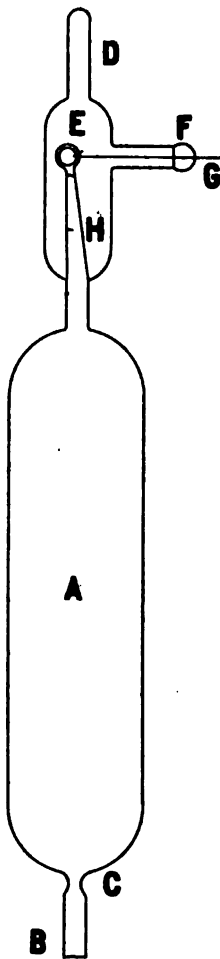
Received May 31, 1915.

The reduction of sulfur dioxide to sulfur by carbon monoxide is a reaction of great technical, as well as scientific, importance. From the free energy of this reaction the free energy of formation of sulfur dioxide could be obtained immediately. Any attempt, however, to determine

the conditions of equilibrium in this reaction is complicated by the formation of carbon oxysulfide, whenever carbon monoxide and sulfur are heated together. Before attacking the former problem it is therefore necessary to determine the free energy of the latter reaction.

The reaction between carbon monoxide and sulfur to give carbon oxysulfide was shown by v. Than¹ to occur at a temperature corresponding to dull red heat. Later, Witzek² found evidence of a dissociation of the oxysulfide at as low a temperature as 300° C. This work seemed to indicate that the equilibrium $\text{CO} + \text{S} = \text{COS}$ might be attained within a reasonable time at moderately low temperatures.

Sulfur and carbon monoxide were heated together in a glass bomb of special design, shown in the accompanying figure. The special apparatus, DEFGH, having been sealed to the large tube A, the sulfur was placed in the latter before drawing down at C and joining to the tube B. The tube B was then attached to the vacuum pump and to the CO reservoir. After exhaustion, the bomb was filled with CO at a pressure a little below one atmosphere, the pressure and temperature were determined, and the tube B was drawn off at C. The bomb was then heated at the desired temperature long enough to insure the establishment of equilibrium and then cooled rapidly in a current of air. The end of the tube D was then cut off and it was joined to the vacuum pump and to the apparatus in which the gas was to be analyzed. After exhausting the chamber E, the platinum wire G and lead glass enamel F were heated to the softening point of the enamel. The wire G was then drawn out sufficiently to break the inner tube H where a file mark had previously been made. By this means the contents of the tube A could be brought directly into the analyzing apparatus without any contamination with air or rubber. This apparatus will doubtless prove convenient in many other experiments of a similar character.



After the gas had been removed from A to the analyzing apparatus by a mercury pump, the volume of A was determined. It was usually about 100 cc.

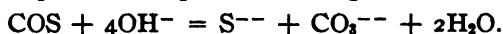
¹ v. Than, *Lieb. Ann. Suppl.*, 5, 236 (1867).

² Witzek, *J. Gasbeleuchtung*, 46, 21 (1903); Abegg, *Handbuch der anorgan. Chemie*, III, p. 207.

The sulfur used was prepared from Kahlbaum's crystallized product by boiling it *in vacuo* to remove traces of CS_2 . Enough sulfur was taken to provide an excess of liquid sulfur at the temperature of the reaction. The carbon monoxide was prepared from oxalic acid and concentrated sulfuric acid. The carbon dioxide and water were carefully removed with suitable absorption bulbs and the CO was drawn into a large glass container from which it could be transferred to the reaction bomb. All connections were of glass and the apparatus and generator were completely freed from air at the outset.

The reaction was carried on in a vapor bath of boiling diphenylamine at 302° . This substance carbonizes gradually, but this was found to have little, if any, effect upon the temperature of the vapor.

In the first experiments (Expts. 2 and 5 referred to below) the gas from the reaction bomb was pumped directly into a bulb containing concentrated alkali and allowed to stand for a sufficient time to absorb all the COS.¹ The absorption takes place according to the reaction

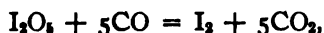


Into this absorption bulb an excess of hydrochloric acid and a known volume of a standard solution of iodine were allowed to enter. This was done in such a way that any H_2S set free by the acid would remain in the bulb and be later oxidized by the iodine. The whole solution was then withdrawn from the bulb and the excess iodine titrated against standard thiosulfate solution.

It was planned to determine the amount of CO in the gas left unabsorbed, by the ordinary methods of gas analysis, but the first experiments showed the amount of CO, remaining uncombined with sulfur, to be less than 1% of the initial CO. In order, therefore, to provide for a satisfactory determination of this gas it was necessary to adopt a different procedure. Therefore in the later experiments (Nos. 19, 20 and 22) the gas from the reaction bomb was drawn into a bulb immersed in liquid air and after a few minutes the uncondensed gas was drawn off. To avoid retention of CO in the solidified gases these were vaporized and once more solidified in liquid air. The total uncondensed gas was pumped into a separate reservoir over mercury and the gases which had been solidified were analyzed for COS as before. Owing to the fact that COS, as well as other substances like CS_2 and CO_2 , which might have been expected to form during the reaction, exert very little vapor pressure at the temperature of liquid air, it was supposed that the total volume of uncondensed gas would represent the amount of CO left in the reaction. In order, however, to make a specific analysis for CO, after trying several unsuccessful methods, a method was adopted which has frequently been

¹ At ordinary temperatures any CS_2 which might have been formed in the reaction would not react appreciably with the alkali,

used for the determination of small amounts of CO in air. The residual gas was mixed with a large volume of air and slowly drawn through a spiral containing iodine pentoxide at 150° and then into absorption bulbs containing KI dissolved in pure water. The reaction is



and experiments made with known quantities of pure CO gave excellent check analyses.

When, however, this method was applied to the uncondensed gas from the reaction bomb, a very mysterious effect was observed. The brown color of iodine appeared at first in the absorption bulbs but later disappeared and the spaces above the liquid were filled with white fumes. At first this phenomenon was attributed to COS and in later experiments greater pains were taken to insure the efficiency of the liquid air condensation, but the same phenomenon persisted. It evidently was due to some gas which could be formed from carbon, oxygen and sulfur and possessing an appreciable vapor pressure at the temperature of liquid air. We were thus led to suspect the presence of a monosulfide of carbon, CS, which presumably would have a boiling point not much higher than that of CO. This suspicion was confirmed when we found that Baudrimont¹ had actually prepared this gas by heating CS₂ and CO together. In our experiments there was evidence that an appreciable amount of CS₂ was formed, presumably from the reaction $2\text{COS} = \text{CO}_2 + \text{CS}_2$. It seemed, therefore, highly probable that the gas CS was responsible for the difficulties in the analysis and steps were therefore taken to remove it from the CO.

From the mixture of CS and CO, the former gas should be removed by a hot metal like copper. The mixture was, therefore, pumped into a glass tube, in the center of which a platinum wire was stretched, by means of a platinum spring, between platinum hooks sealed through the tube. Before use the platinum wire was plated electrolytically with copper and after the introduction of the gas an electric current was sent through this copper plated wire, heating it to dull redness. The copper appeared to react rapidly with the gas, becoming covered with a black coating of sulfide. After this treatment the gas was mixed with air and the analysis for CO continued as before. This procedure completely eliminated the bleaching of the iodine and the formation of the white fumes.

Owing to the very considerable experimental difficulties of manipulation and analysis, only a few of the numerous experiments which were made led to final results of value. In fact, there was no single tube which was successfully analyzed for both COS and for CO, but owing to the complete similarity of the various experiments this fact need not diminish our confidence in the results which were ultimately obtained. It may

¹Baudrimont, *Compt. rend.*, 44, 1000 (1857).

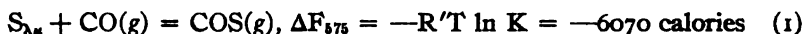
be added that a number of the experiments which are not included in our final summary furnish satisfactory checks of the results here given.

Table I summarizes the results of the five experiments upon which we may place complete reliance.

TABLE I (302°).

No. of expt....	2	5	19	20	22	Aver.
Time in hours..	189	72	120	120	100	
Mols CO (initial).....	0.005944	0.004375	0.004829	0.005279	0.004943	
Mols CO per mol CO (initial).....			0.00419	0.00407		0.00413
Mols COS per mol CO (initial).....	0.8181	0.8525			0.8185	0.8297

The equilibrium constant $K = [\text{COS}]/[\text{CO}]$ can be obtained from this table with an error apparently not exceeding a few per cent. Using the average values given above, $K = 0.830/0.00413 = 201$. Writing $S_{\lambda\mu}$ to represent liquid sulfur in its equilibrium condition, we may write for the reaction



In order to obtain a similar equation involving sulfur in its standard state (rhombic), we may use the values of Lewis and Randall.¹ According to their Table I we may write for $S_{\lambda} = S_{\lambda\mu}$; $\Delta F_{575} = -44.5$. And, from their Equation 9, $S_R = S_{\lambda}$; $\Delta F_{575} = -294$. Adding these equations,



Unfortunately it is not possible, in the customary way, to calculate from this figure the value of ΔF at another temperature, owing to the very conflicting values of the heat of this reaction given by Thomsen and Berthelot. According to the former, the heat evolved in this reaction is 8030 cal., while according to the latter it is -6200 cal., a difference of over 14,000 cal. Both of these values are for rhombic sulfur at room temperature. For liquid sulfur at the temperature of our experiments these figures should be about 2000 cal. greater, according to the data given by Lewis and Randall, that is, approximately +10000 and -4000. We should expect the ratios of COS to CO to diminish with increasing temperature according to Thomsen, and to increase with increasing temperature according to Berthelot.

It seemed desirable, therefore, to attempt a determination of this equilibrium at some other temperature. A higher temperature seemed out of the question, since such evidence as we possessed regarding the

¹ THIS JOURNAL, 36, 2468 (1914).

speed of the reaction indicated that at a temperature much higher than 300° it would be impossible to cool the reacting mixture with sufficient rapidity to prevent a shift of equilibrium. Experiments were therefore made at 260° with the same kind of apparatus in a thermostat of fused nitrates, the construction of which has been described by Lewis.¹ Unfortunately, owing to difficulties in the central power system, the thermostat was not entirely satisfactory and the experiments about to be described must be regarded as preliminary in character.

Table II shows the results of five experiments. The first three tubes were in the thermostat from 21 to 23 days, but in all three cases the temperature fluctuated very greatly at the beginning, and before the tubes were removed, constant temperature was maintained for only seven days in the first case, eight days in the second and five days in the third. But a later experiment showed that these intervals could hardly suffice for a complete establishment of equilibrium. With the possible exception, therefore, of the second experiment these three may be disregarded. The fifth experiment was in every way satisfactory and constant temperature was maintained for seventeen days. In the fourth constant temperature was maintained but the tube was left in the thermostat only five days. The large amount of CO left in this case shows conclusively that this length of time is insufficient for the establishment of equilibrium.

TABLE II (260°).

No. of experiment.....	1	2	3	4	5
Time in days.....	22(7)	23(8)	21(5)	5	17
Mols CO (initial).....	0.00534	0.00550	0.00508	0.00842	0.00789
Mols CO per mol CO (initial)...	0.00118	0.00168	0.00097	0.0216	0.00171
Mols COS per mol CO (initial)...	0.8015	0.6990		0.7725	0.7402

It is evident that with diminishing temperature the equilibrium is shifted in favor of CO. In the fifth experiment there can be little doubt that equilibrium was reached, and except that, for reasons which will be explained presently, the amount of COS found in this experiment may be 2% or 3% low, this experiment may be regarded as a sufficient basis for a provisional calculation of the equilibrium constant at this temperature. In this case $K_{583} = 0.74/0.0017 = 435$.

If now, by the van't Hoff equation, we use the two values of K to determine the heat of the reaction, we find -11000 instead of -4000 from Berthelot and $+10000$ from Thomsen. This indicates that Thomsen's value, at least, is erroneous. We must not, however, lay too much stress upon the value which we have obtained from the van't Hoff equation, used over a small range of temperature, with one equilibrium constant obtained from a single measurement. It seems therefore desirable to post-

¹ THIS JOURNAL, 28, 1380 (1906).

pone the calculation of the free energy of this reaction at standard temperature until we have more reliable calorimetric measurements. Such measurements are now being made in this laboratory.

It will have been noticed that a considerable part of the gas left in the tubes after heating was neither COS nor CO. Thus, at 302°, about 0.5% of the CO remained as such, and 83% was used in forming COS. Judging from the volume of the residual gas and from the amount of CO determined by analysis, the amount of CS₂ was approximately equal to that of CO. This leaves 16% of the gas unaccounted for. This was assumed to be a mixture of approximately equal parts of CO₂ and CS₂. Each of the three reactions, $\text{CO} + \text{S} = \text{COS}$, $2\text{COS} = \text{CO}_2 + \text{CS}_2$ and $\text{CS}_2 = \text{CS} + \text{S}$ leads to no change in the number of mols of gas when the temperature is sufficiently low for the condensation of the sulfur, but not low enough to condense CS₂. In fact, the final volume of the reacting mixture was always 1–2% lower than that of the CO used. This was attributed to the fact that the resulting gases are less perfect than CO. It would have been desirable to analyze for CO₂ and CS₂, but this would have added almost insuperable difficulties to the already very difficult analytical procedure. It did seem worth while, however, to satisfy ourselves as to the general correctness of our assumption. In the last two experiments at the lower temperature that portion of the gas which was frozen out by liquid air was transferred to a tube immersed in liquid alcohol at a temperature of –80°. The gas was then pumped out from this cold chamber until the pressure was 0.5 mm. of mercury. This gas was analyzed as before for COS, and the liquid which remained was afterwards transferred to a small tube which was sealed off and weighed. This liquid was unquestionably CS₂. In Expt. 4 the weight of this liquid corresponded to 0.073 mols of CS₂ per mol of CO (initial). The boiling points of CS₂, COS and CO₂ are, respectively, 46°, –47.5° and –80°. The separation of COS from CS₂ could hardly be expected to be quantitative and it seemed probable that in the experiment just mentioned some of the CS₂ was pumped off. In Expt. 5, therefore, the gases were pumped off only until the pressure was about 1 mm. The amount of liquid left in this case corresponded to 0.155 mol CS₂ per mol CO (initial). In this case it is almost certain that some of the COS remained with the CS₂.

It seems pretty certain, therefore, that of the 20% of gas which was not CS, CO and COS, approximately one-half is CS₂. Presumably the other half is CO₂, and if so we can estimate roughly the equilibrium constant for the reaction $2\text{COS} = \text{CO}_2 + \text{CS}_2$ as

$$K_{533} = [\text{CO}_2][\text{CS}_2]/[\text{COS}]^2 = 0.10 \times 0.10/(0.79)^2 = 0.016.$$

A calculation of the measurements at the higher temperatures, based upon similar assumptions, gives

$$K_{575} = 0.08 \times 0.08/(0.83)^2 = 0.009.$$

Now, these constants could be calculated from our value of the free energy in the reaction $\text{CO} + \text{S} = \text{COS}$, and the equation given by Koref¹ for the dissociation of CS_2 as a function of the temperature, together with the free energy tables given by Lewis and Randall.² This calculation, which we shall not reproduce here, would lead to the conclusion that at the temperature of our experiments CO_2 and CS_2 would be present in larger amounts than COS . Koref used a heat of dissociation of CS_2 calculated from his own equilibrium measurements and this value would be largely affected by small errors in the degree of dissociation. That such errors were probable is evident from the fact that Koref made no allowance for the formation of CS , nor for such other substances as may be formed by heating CS_2 .³

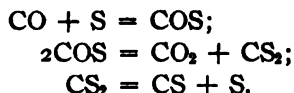
We may note, in passing, that the reaction $2\text{COS} = \text{CO}_2 + \text{CS}_2$ appears to be much more rapid than the reaction $\text{CO} + \text{S} = \text{COS}$ at the temperatures of our experiments.

Finally, although CS was not directly determined in any of our experiments, we may give an approximate estimate of the equilibrium constant in the reaction $\text{CS}_2 = \text{CS} + \text{S}_{\text{vapor}}$. Taking the amount of CS as equal to that of CO , we have $K_{478} = [\text{CS}]/[\text{CS}_2] = 0.004/0.08 = 0.05$.

Until more reliable calorimetric measurements are available we shall not attempt to reduce any of these results to standard temperature.

Summary.

When carbon monoxide and sulfur are heated together at 250° to 300°C ., carbon oxysulfide, carbon dioxide, carbon disulfide and carbon monosulfide are formed by the reactions:



The equilibrium in the first reaction was determined at 302° and less reliably at 260° . Approximate values were obtained for the equilibrium constants of the other two reactions.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE RUBIDIUM ELECTRODE.

By GILBERT N. LEWIS AND WILLIAM L. ARGO.

Received June 9, 1915.

The method used by Lewis and Kraus, and Lewis and Keyes for the determination of the electrode potential of sodium,⁴ potassium⁵ and

¹ *Z. anorg. Chem.*, 66, 73 (1910).

² *THIS JOURNAL*, 36, 2468 (1914); and 37, 458 (1915).

³ See Arctowski, *Z. anorg. Chem.*, 8, 314 (1895).

⁴ *THIS JOURNAL*, 32, 1460 (1910).

⁵ *Ibid.*, 34, 119 (1912).

lithium¹ seems at first sight inapplicable to the remaining two alkali metals, rubidium and cesium. That method consists in determining first the normal electrode potential of a dilute amalgam of the metal towards an aqueous solution of the ion of the metal, and second the difference in potential between the amalgam and the pure metal in a liquid amine solution of a salt of the metal in question. Potassium and sodium iodides were used in ethylamine and lithium iodide in propylamine. But rubidium iodide is so nearly insoluble in propyl and ethyl amines as to have no measurable electrical conductivity, while the metal rubidium is freely soluble in methylamine and ammonia. Rubidium amide was likewise found too little soluble in ethylamine and although there may be some rubidium salt of an oxygen acid which would dissolve more freely, such a salt would doubtless react with the metal.

Choice of Solvent: Preparation of Materials.

It seemed possible that by adding some inert solvent to ammonia a mixture might be obtained which would not dissolve rubidium but which would dissolve rubidium iodide sufficiently to permit measurements of electromotive force. Pentane was the first substance tried, but it was soon evident that neither this nor any similar substance would serve; for, although pentane and ammonia are miscible in all proportions, a small amount either of the iodide or of the metal sufficed to cause a separation into two liquid phases, and in the phase consisting chiefly of pentane neither iodide nor metal was dissolved to any measurable extent.²

Mixtures of ethylamine and ammonia were next investigated and found to offer an adequate, if not a completely satisfactory, solution of the problem. The solubility of both metal and iodide changes very markedly with small changes in the composition of the mixture. It was therefore necessary to prepare mixtures of accurately known composition. The anhydrous ethylamine was kept in a reservoir of the type described by Lewis and Kraus. The ammonia was kept in the form of a Divers solution (a saturated solution of ammonium nitrate in liquid ammonia), both the nitrate and the ammonia having been dried with great care. The two components of the mixed solvent were measured separately as vapors in bulbs of known volume at measured pressures, and were then condensed at a temperature of about -80°C . in the apparatus in which it was to be used.

In order to test roughly the conductivity of a saturated solution of rubidium iodide as a function of the composition of the solvent, a glass tube about 5 mm. in diameter with two platinum electrodes (about 0.5 sq. mm. in area and 5 mm. apart) was used. A small crystal of rubid-

¹ THIS JOURNAL, 35, 340 (1913).

² Sodium and not rubidium was the metal used in this experiment.

ium iodide was placed in this cell, which was then exhausted while being heated nearly to the softening point of the glass. After cooling, the solvent was allowed to enter. A potential of 110 volts was then applied across the two electrodes and the current roughly determined. Table I gives the results of four such experiments.

TABLE I.

Mol per cent. ammonia.....	7.9	9.0	11.0	13.4
Amperes (with 110 v.).....	0.0002	0.0005	0.0007	0.0015

Similar experiments were made to determine the solubility of rubidium, which could be estimated roughly from the color. The solvent containing 7.9 mol per cent. of ammonia gave a very pale blue solution which may be estimated to be not over 0.001 *M* with respect to the metal. With increasing percentage of ammonia the blue color becomes more intense and at 13.4 mol per cent. of ammonia a second liquid phase of metallic appearance is formed. Except in one case, the solvent containing 7.9 mol per cent. of ammonia was used in the following experiments:

The rubidium amalgam was prepared by the electrolysis of an aqueous solution of Kahlbaum's rubidium carbonate with a mercury cathode. The amalgam thus formed was freed from traces of water and solid impurities, and collected in an exhausted reservoir. According to two analyses, 1 g. of the amalgam contained 2.696×10^{-5} and 2.701×10^{-5} equivalents of rubidium. The average taken is 2.698×10^{-5} .

The metallic rubidium obtained from Kahlbaum was used in all but one of the experiments. In that one, the rubidium was prepared by distilling a mixture of metallic calcium and rubidium iodide in an evacuated quartz vessel.

All measurements were made in an oil thermostat at 25° C.

Electromotive Force of the Rubidium—Rubidium Amalgam Cell.

The first cell used was similar to the one used by Lewis and Kraus in the case of sodium. A small amount of rubidium iodide, carefully dried, was introduced into the cell which was then exhausted. The rubidium was introduced in the molten state through a fine capillary. The amalgam from its reservoir was allowed to run into the other side of the H cell and the mixed solvent was introduced as previously described. The solvent was found to be too rich in ammonia, since it not only formed a deep blue solution of rubidium but also produced a concentrated layer, of metallic appearance, over the rubidium electrode. The electromotive force of this cell was about 0.9 volt, but inconstant. We attempted to reduce the concentration of ammonia in the following manner: A side tube which had been added to the cell for the original condensation of the solvents was now cooled until a certain amount of ammonia, which is far more volatile than the ethylamine, was condensed in it. This

tube was then sealed off and the cell being placed in the thermostat showed only a pale blue color. The electromotive-force readings then obtained are given in Table II (Cell 1). The gradual fall in potential which was noticed in this and all other cases is undoubtedly to be attributed in part to a slow increase in the concentration of the amalgam, which is due to a transference of the metal from the rubidium electrode through the solution.

In all the following experiments the solvent contained 7.9 mol per cent. of ammonia. Experiments with Cell 1 showed the desirability of producing a fresh surface of rubidium during the electromotive-force

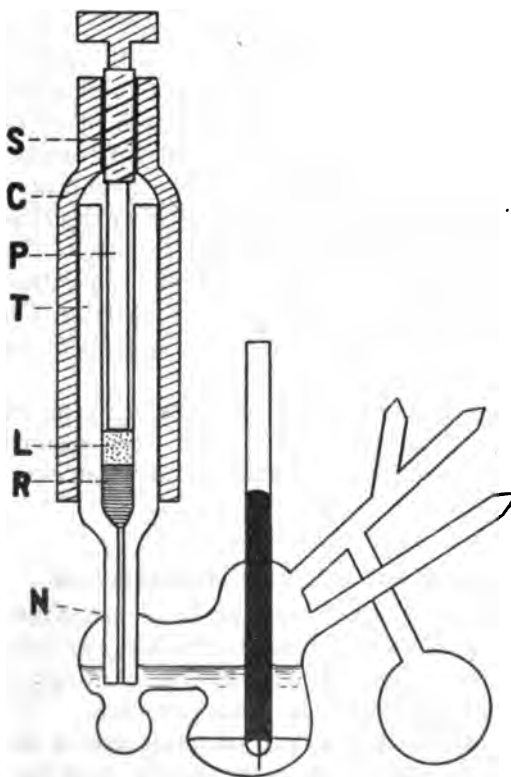


Fig. 1.

measurements. An arrangement similar in principle to a sodium press was therefore added to the cell. It is shown in Fig. 1. A heavy-walled glass tube (T) was drawn out to a capillary, also heavy-walled, and sealed into the top of one arm of the cell at (N). Over this tube was fitted a brass collar (C), threaded at the upper end to admit the screw (S). The rubidium was introduced and forced quickly down to the bottom of the tube to the position (R). A leather plug (L) and a brass rod (P) were then inserted. By turning the screw (S) any desired pressure within the limits of strength of the glass cylinder could be exerted evenly on the rubidium. Being quite soft at 25° , it flowed gradually through the capillary and emerged at the open-

ing in the form of a bright "worm," free from oxide coating. For electrical connection a thin platinum wire was inserted through the chamber and a short distance into the capillary before the rubidium was introduced.

Cells 2 and 3 gave results which do not contribute much to our knowledge of the electromotive force in question, since in Cell 3 we know that during the manipulation a certain amount of metallic rubidium was car-

ried into the amalgam,¹ and there was a strong suspicion that this was also the case with Cell 2. The effect of concentrating the amalgam is obviously to diminish the observed e. m. f. These cells, however, furnished valuable experience in manipulation and also offered an opportunity to determine the result of stirring the electrolyte, and of renewing the rubidium surface. It is for this reason that these cells are included in Table II. The cells were stirred before nearly every reading and the rubidium surface was renewed after readings 1 and 4 with Cell 2 and after reading 6 with Cell 3. The results show that little, if any, effect is produced by either of these changes.

After the experience gained with these cells, a new cell, No. 4, was filled and manipulated with great caution, and gave results so satisfactory that its electromotive force, which agrees with that obtained in Cell 1, may be confidently taken as the true electromotive force between rubidium and the rubidium amalgam. It is to be noted that Kahlbaum's rubidium was used in Cell 1 and our own preparation in Cell 4. Allowing for a possible slight diminution in electromotive force while the cell was being placed in the thermostat, we may take 1.0745 volts as the final value. The last figure is probably not significant.

TABLE II.

Cell 1.		Cell 2.		Cell 3.		Cell 4.	
Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)
0	1.0742	0	(1.0695)	0	(1.0629)	0	1.0742
35	1.0735	2	(1.0697)	8	(1.0631)	5	1.0742
45	1.0736	25	(1.0695)	13	(1.0628)	8	1.0745
60	1.0733	35	(1.0696)	14	(1.0629)	10	1.0741
82	1.0732	100	(1.0697)	30	(1.0629)	12	1.0740
92	1.0731	175	(1.0694)	60	(1.0629)	14	1.0738
125	1.0724	190	(1.0700)	817	(1.0620)	25	1.0734
225	1.0720	203	(1.0693)	960	(1.0621)	30	1.0738
241	1.0719					31	1.0737
729	1.0685					33	1.0738
						35	1.0736

There may be some question as to the influence of the solubility of rubidium upon this electromotive force, but it is to be observed that the blue color did not extend completely from one electrode to the other, since the solution immediately above the amalgam was always colorless. We believe that the small amount of metal in solution produced no appreciable effect upon the initial electromotive force, especially as the concentration of rubidium was not the same in Cells 1 and 4, which gave the same e. m. f.

¹ Owing to the extremely poor conductivity of the solution it was necessary to design the cell so that very little space intervened between the two electrodes.

The Normal Electrode Potential of the Rubidium Amalgam.

The potential of the rubidium amalgam in a 0.1 *M* aqueous solution of rubidium hydroxide was measured against the normal calomel electrode in the same type of apparatus as was used for the other alkali metals. The cell consisted of the chain, Rb amalgam, RbOH (0.1 *M*), RbCl (0.1 *M*), N. E. The rubidium hydroxide was prepared by treating some of the amalgam with pure water; the rubidium chloride, by mixing a solution of rubidium iodide with an ammoniacal solution of silver chloride, filtering, evaporating to dryness, and heating to drive off ammonium salts.

A device which has been developed in this laboratory, and which will be described in another place, allowed repeated renewals of the liquid junction between RbCl and RbOH. The amalgam surface, which also could be renewed at will, reacted far more rapidly than in the case of the amalgams of the other alkali metals. This may be an intrinsic property of rubidium amalgam, or it may be due to the greater difficulty of preparing pure salts owing to the small amount of the expensive material used.¹ After forming a new amalgam surface in the electrode chamber, the electromotive force would fall, slowly at first, and then more rapidly. During the first minute the change would amount to 0.1 to 0.2 millivolt. Two series of measurements were made several weeks apart and with different normal electrodes. These two series are given in Table III. Before each measurement both the amalgam surface and the liquid junction were changed. The measurements do not show as high a degree of constancy as might have been hoped for, but owing to the constantly changing conditions the variations are at a maximum, and we may therefore be sure that the average result, 2.1805 volts, cannot be seriously in error.

TABLE III.

Series 1. E.	Series 2. E.	Series 1. E.	Series 2. E.
2.1810	2.1794	2.1802	2.1806
2.1800	2.1808	2.1805	2.1812
2.1796	2.1815	2.1804	2.1811
2.1802	2.1808	2.1805	2.1808
2.1806	2.1800	2.1805	2.1802
		Average, 2.1804	2.1806

Since the mobility of Rb^+ is almost exactly the same as that of K^+ , the liquid potential RbOH (0.1 *M*), RbCl (0.1 *M*) may be taken the same as that of the corresponding junction with potassium salts, namely,

¹ The extraordinary effect of small impurities in accelerating the reaction between an amalgam and an aqueous solution has been shown by Walker and Patterson, *Trans. Am. Electrochem. Soc.*, 3, 185 (1903); and by Lewis and Jackson, *Z. phys. Chem.*, 56, 198 (1906).

0.0165 volt¹ at 25° C. Likewise, since it is the custom to neglect the potential KCl (0.1 *M*), KCl (1.0 *M*), we may neglect the equal potential RbCl (0.1 *M*), KCl (1.0 *M*). Thus, for the above cell without liquid potentials we would have Rb amalgam, RbOH (0.1 *M*) || N. E.; $E = 2.1970$.

In order to calculate the potential of the rubidium amalgam against Rb^+ at (hypothetical) molal concentration, we shall assume the "corrected" degree of dissociation of RbOH (0.1 *M*), in the absence of any direct measurements, to be the same as that of KCl (0.1 *M*), namely 0.76.² We have, therefore, Rb amalgam, RbOH (0.1 *M*) || Rb^+ (1 *M*), Rb amalgam, $E = -0.05915 \log 0.076 = 0.0662$ volt. Subtracting this from the above value we have Rb amalgam, Rb^+ (1 *M*) || N. E.; $E = 2.1308$ volts.

Electrode Potential of Rubidium and of Lithium, Sodium and Potassium.

By combining the normal electrode potential of the rubidium amalgam with the difference in potential between rubidium and the amalgam we find Rb, Rb^+ (1 *M*) || N. E.; $E = 2.1308 + 1.0745 = 3.2053$ volts. We shall take, therefore, as the normal electrode potential of rubidium at 25° against the normal calomel electrode, 3.205 volts.

There seems to be little hope at present of determining the potential of cesium by the same method, for in the solvents which we have investigated the metal is more soluble and the iodide less soluble than in the case of rubidium. We may therefore summarize at this point the results obtained for the four alkali metals.

In Table IV the second column gives the normal electrode potential measured against the normal calomel electrode. The values previously given for sodium and potassium were based upon the old international volt and upon the assumption that the degree of dissociation of NaOH (0.2 *M*) is 0.828 and that of KOH (0.2 *M*) is 0.830. We have recalculated these values in terms of the new international volt and on the assumption that the "corrected" degree of dissociation is the same as that of KCl (0.2 *M*), namely, 0.71. This assumption may not be entirely correct, but it gives the best estimate which is possible at present. The new value of the corrected degree of dissociation also changes the lithium potential by 0.0007 volt. The third column gives the normal electrode potentials of these elements against the normal hydrogen electrode taken as zero. This column is obtained by subtracting 0.2776 from the figures of the preceding column.³ The potentials of the

¹ See Lewis and Randall, *THIS JOURNAL*, 36, 1969 (1914).

² The corrected degrees of dissociation here employed differ slightly from those obtained by Lewis, *THIS JOURNAL*, 36, 1969 (1914). The revision of these values will be discussed in another paper.

³ Lewis and Randall, *Loc. cit.*

alkali metals follow a curious order, namely, lithium, rubidium, potassium, sodium. It is interesting, however, to observe that this is the order of the heats of formation of the several ions in aqueous solution. In order to illustrate this fact the heat of formation of the chlorides of the four metals in aqueous solution are given in the last column.

TABLE IV.

	Potential against N. E.	Potential against hydrogen.	Heat of formation of chlorides.
Li.....	3.305	3.027	102000
Rb.....	3.205	2.928	101000
K.....	3.203	2.925	101000
Na.....	2.993	2.715	96000

The heat of formation of aqueous cesium chloride is given as 105,000 calories, and if this figure is correct we might predict the potential of cesium to be higher than that of any of the other alkali metals.

We wish to express our indebtedness to the Bache Fund of the National Academy for financial aid in this series of investigations.

BERKELEY CAL.

[CONTRIBUTION FROM CHEMICAL LABORATORY, BRYN MAWR COLLEGE.]

A STUDY OF ALCOHOLIC SOLUTIONS OF CADMIUM IODIDE.

BY FREDERICK H. GETMAN AND VERNETTE L. GIBBONS.

Received June 11, 1915.

I. Conductance.

The data for the conductance of cadmium iodide in alcoholic solutions was found to be very meager. Zelinsky and Krapiwins,¹ and Jones and Carroll,² measured the conductance of various solutions of cadmium iodide with methyl alcohol as the solvent, but there is great disagreement between the two sets of values, and when plotted neither set gives a smooth curve. Jones and Carroll² also measured the conductance of cadmium iodide with ethyl alcohol as the solvent. As far as recorded, only one series of measurements was made in each case. It therefore seemed advisable to redetermine the conductance of cadmium iodide in methyl and ethyl alcoholic solutions.

In the work, the results of which are here given, extreme care was taken to avoid, as far as possible, all known sources of error. The purest cadmium iodide obtainable was powdered and allowed to stand in a desiccator over phosphorous pentoxide for several days. The alcohols were dehydrated over pure lime for several weeks and then distilled, using a fractionating column and collecting in a dry receiver protected from the gases and moisture of the atmosphere by means of a soda-lime tube. The boiling point of the ethyl alcohol was 77.3° at 743.1 mm. and the boiling point

¹ *Z. physik. Chem.*, 21, 35-52 (1896).

² *Bull. Carnegie Inst.*, 80, 41-73 (1907).

of the methyl alcohol was 64.2° to 64.5° at 752 mm. The measurements of the electrical conductance were made by means of the well-known Kohlrausch apparatus, a Leeds and Northrup cylindrical bridge being used. The cell was of the ordinary Arrhenius form, closed with a tight-fitting ebonite cover. Its constant was found to be 16.27 and did not alter during the progress of the conductance measurements.

The solutions were made up either by direct weighing or by dilution from a stronger solution. The flasks and burets used were carefully calibrated. In several cases duplicate measurements were made with solutions made up by direct weighing and by dilution from a more concentrated

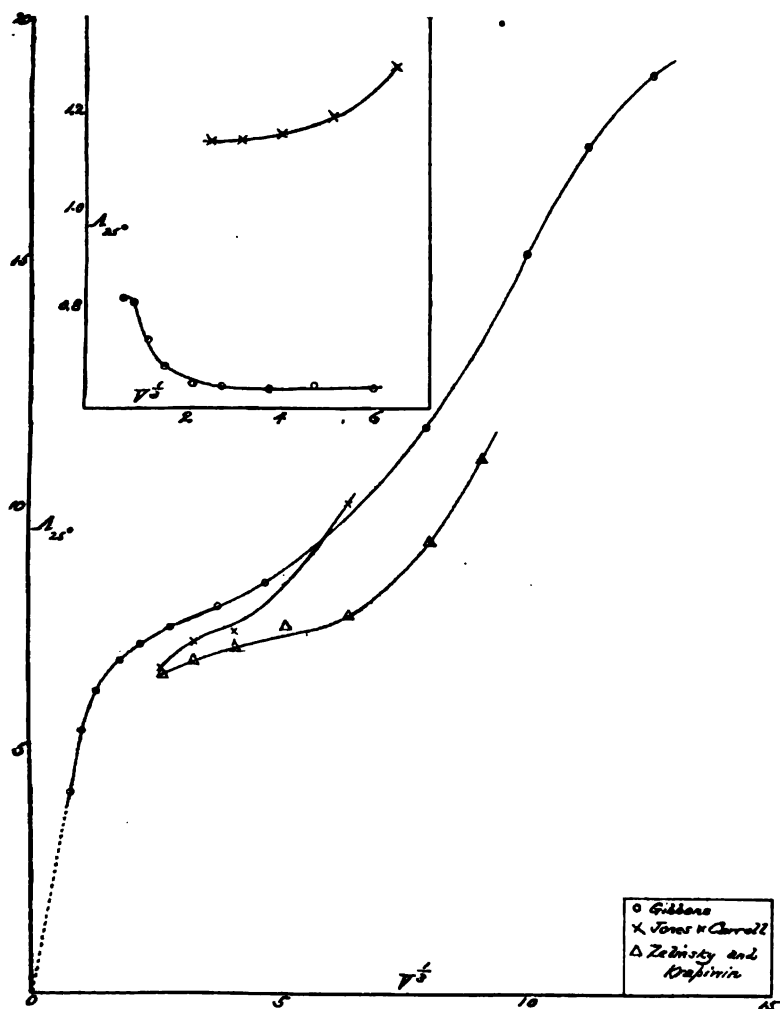


Fig. 1.

solution, and in no case was a solution diluted more than twice. The cell was always filled twice and duplicate readings taken, so that at least four measurements were made with each solution. These results corroborate each other and the curves are quite smooth, as is shown by Fig. 1, plotted from the data given in Table I.

TABLE I.

SOLUTIONS IN METHYL ALCOHOL.			SOLUTIONS IN ETHYL ALCOHOL.		
m.	v.	$\Delta 25^\circ$.	m.	v.	$\Delta 25^\circ$.
2.0	0.5	4.14	2.0	0.5	0.825
1.0	1	5.40	1.0	1	0.817
0.5	2	6.20	0.5	2	0.740
0.2	5	6.82	0.25	4	0.684
0.1	10	7.14	0.1	10	0.650
0.05	20	7.49	0.05	20	0.644
0.02	50	7.89	0.02	50	0.639
0.01	100	8.39	0.01	100	0.646
0.005	200	9.33	0.005	200	0.640
0.002	500	11.58			
0.001	1000	15.14			
0.0007	1428.6	17.35			
0.0005	2000	18.82			

The conductance curve for methyl alcoholic solutions of cadmium iodide is complicated, indicating complex conditions in the solutions; the curve for the ethyl alcoholic solutions is the exact reverse of what one would naturally expect. It has been shown by Jones and Carroll¹ that when water is mixed with the alcohol as a solvent, the conductance of the solute is increased. It is obvious therefore, that the lower values obtained by us for the ethyl alcoholic solutions cannot be caused by the absorption of moisture by the solutions. The values obtained by us with solutions in methyl alcohol are, it is true, higher than those obtained by the other observers, but the fact that several points on the curve were corroborated by measurements of solutions made up by direct weighing and by dilution confirms the accuracy of the work. In the case of the 0.05 *N* concentration three solutions were used; one made up from a *N* solution and two by direct weighing, using alcohol obtained by two different distillations.

Jones and Getman² measured the molecular rise in the boiling point of ethyl alcoholic solutions of cadmium iodide. If molecular association occurs, as was plainly indicated by their results, the degree of association would probably be greater at 25° , the temperature at which the conductance measurements were made, than at the boiling point of the solvent. If one studies the plotted values for methyl alcoholic solutions of cadmium iodide given by Zelinsky and Krapivin and Jones and Carroll (Fig. 1), one sees that although the values lie lower than those given by us, there is,

¹ *Bull. Carnegie Inst.*, 80, 41-73 (1907).

² *Am. Chem. J.*, 31, 303-359 (1904).

in general, a similar trend or complexity, which partially explains the lack of smoothness observed. By comparing the curves here given with the conductance curves for silver nitrate in nonaqueous solutions given by Gibbons and Getman,¹ one sees certain similarities. The curve for the conductance of cadmium iodide, when ethyl alcohol is the solvent, is quite analogous to the middle portion of the curve for the conductance of silver nitrate, when aniline was the solvent, and an upward trend is noted in the curves of conductance of silver nitrate in acetone, in pyridine and in aniline, just as is noted in the more dilute concentrations of cadmium iodide when methyl alcohol is the solvent. Just as the anomalies in the conductance curves of silver nitrate have been explained on the basis of complexes existing in the solution, so may also be explained the anomalies here observed with alcoholic solutions of cadmium iodide.

That molecular complexes do exist in both aqueous and nonaqueous solutions of cadmium iodide is shown by the determination of the transport numbers, the molecular depression of the freezing point, and the molecular elevation of the boiling point. Hittorf² measured the transport numbers for cadmium iodide in ethyl and amyl alcoholic solutions and obtained negative values for the cadmium ion. The values obtained with amyl alcoholic solutions were greater than those obtained with ethyl alcoholic solutions. Jahn³ and his students worked with cadmium iodide in aqueous solutions and found the transport number for the cation practically constant for concentrations between 0.005 *N* and 0.2 *N*, while for higher concentrations the value diminished and at a concentration of 0.5 *N* the transport number for the cation was negative, *i. e.*, -0.0003. Hittorf,² and Noyes and Falk⁴ considered these negative values for the transport number of the cation as proof of the existence of complex ions in the solutions. McBain,⁵ after taking into account all the data of measurements of conductance, freezing point, and transport numbers, concluded that in a 0.1 *N* aqueous solution about 80% of the molecules were undissociated CdI_2 , and that about half the anion was CdI_2^- . From the values of the transport numbers, it is clear that for any given concentration the ethyl alcoholic solution will contain a larger proportion of complexes, both molecules and ions, than the corresponding aqueous solution, and by analogy it is safe to assume that in a methyl alcoholic solution the proportion of complexes will be between the values for aqueous and for ethyl alcoholic solutions.

In solutions of cadmium iodide in the alcohols several reactions may take place. The complexes C_m may decompose into simpler molecules, or they

¹ THIS JOURNAL, 36, 1630-1655 (1914).

² *Pogg. Ann.*, 106, 551, 554, 558 (1859).

³ *Z. physik. Chem.*, 37, 673-712 (1901).

⁴ THIS JOURNAL, 33, 1460 (1911).

⁵ *Z. Electrochem.*, 11, 222 (1905).

may ionize to form complex ions A' and K' , or the simple molecules may ionize to form simple ions A and K . The form which the conductance curve takes depends entirely upon which of the three reactions predominates. In the more concentrated regions the complexes predominate and in the more dilute regions solvation plays its part. In the case of silver nitrate solutions, the complexes were known to be a combination of solute and solvent, and in the cases where abnormal conductance occurred the solvent had a very low dielectric constant and high viscosity. In the case of cadmium iodide solutions, the complexes are combinations of the molecules of the solute. The conductance of the ethyl alcoholic solutions is extremely weak, which indicates a very slight amount of ionic dissociation. The abnormalities observed in the ethyl alcoholic solution occur in the more concentrated regions, while those observed in the methyl alcoholic solutions occur in the more dilute regions. It would seem therefore, that in the more concentrated ethyl alcoholic solutions the strong associative power of the solute offsets the effect of the moderately high dielectric constant of the solvent. In the more dilute methyl alcoholic solutions, it is possible that the dissociation of the simple molecules into ions predominates and causes the rapid upward slant of the curve. It is also possible that in these dilute solutions solvation plays its part. It is therefore quite apparent that the diminishing conductance with increasing dilution depends upon the complexity of the conducting complexes rather than upon the nature of their components.

II. Density and Specific Refraction.

In 1911-1912 Miss Gilroy,¹ working in this laboratory, made a study of the relation between the density and the refractive index of aqueous solutions of cadmium iodide and calculated the specific refraction according to the Lorentz-Lorenz formula.

$$r = \frac{1}{p} \cdot \frac{n_1^2 - 1}{n_1^2 + 1} \cdot \frac{100}{d_1} - \frac{n_2^2 - 1}{n_2^2 + 1} \cdot \frac{100 - p}{d_2}.$$

(r denotes the specific refraction of the solute at the temperature of the experiment, p the per cent. of solute in the solution, n_1 and n_2 denote the refractive indices and d_1 and d_2 denote the densities of the solution and the solvent, respectively, at 20.5°.) She found the specific refraction at 25° practically constant for the solutions employed (about 0.04 N to 1.5 N).

A similar study of methyl and ethyl alcoholic solutions of cadmium iodide at 20.5° was undertaken. A Sprengel-Ostwald pycnometer of about 10 cc. capacity was used and duplicate measurements were made with each solution. The densities were referred to water at 4°. The refractive indices were measured with the improved form of Pulfrich re-

¹ Getman and Gilroy, *Am. Chem. J.*, 48, 138-145 (1912).

refractometer manufactured by Zeiss. The temperature was kept constant at $20.5^\circ \pm 0.1^\circ$ by means of a Van Aubel thermostat. The light source was a sodium flame. As in the work with aqueous solutions, the Lorentz-Lorentz formula was used for the calculation of the specific refraction, as it was found to give more uniform results.

TABLE II.

Cadmium Iodide in Methyl Alcohol.

m.	%.	d.	n.	r.
0.	0.	0.7942	1.32875	
0.5	11.555	0.8766	1.34300	0.1260
0.2	4.602	0.8269	1.33452	0.1212
0.1	2.301	0.8099	1.33159	0.1258
0.05	1.150	0.8021	1.33016	0.1223
0.02	0.460	0.7969	1.32932	0.1537
0.005	0.115	0.7943	1.32887	0.2920
0.0005	0.012	0.7942	1.32887	0.7270

Cadmium Iodide in Ethyl Alcohol.

0.	0.	0.7891	1.36104	
2.	46.412	1.1068	1.40964	0.1582
1.	23.206	0.9484	1.38517	0.1373
0.5	11.613	0.8688	1.37289	0.1231
0.25	5.802	0.8292	1.36695	0.1142
0.2	4.641	0.8210	1.36559	0.1113
0.1	2.321	0.8052	1.36355	0.1068
0.05	1.160	0.7973	1.36219	0.1004
0.02	0.464	0.7924	1.36148	0.0957
0.01	0.232	0.7911	1.36136	0.0722
0.005	0.116	0.7900	1.36117	0.0833

Plotting the densities and refractive indices of the solutions against the concentrations shows the relationship in each case to be rectilinear. The specific refraction was calculated on the assumption that the volume of the solvent was in each case the same as the volume of the solution. The specific refraction was found to be practically constant for the more concentrated solutions in methyl alcohol, but for the less concentrated solutions the value increased rapidly with dilution. However, in the calculation of the specific refraction of a very dilute solution the sources of error may be very great. The specific refraction of the ethyl alcoholic solutions showed no constancy of value whatever, and instead of increasing with the dilution of the solution it rapidly diminished.

There was a possibility that the error introduced by assuming the volume of the solvent to be the same as the volume of the solution, might explain the difference. If in the one case there was expansion and in the other contraction, when the salt was dissolved, the value of the specific refraction would naturally be effected correspondingly. A determination of the volume changes on dissolving cadmium iodide in the two alcohols

was carried out in the following way: A 100 cc. calibrated measuring flask was weighed, filled to the mark with the pure alcohol at the temperature 20.5° . The weight of the alcohol was determined and the weight of cadmium iodide required to make 100 cc. of a given normality of solution was added to the alcohol in the flask. The expansion or the contraction was noted and its exact amount calculated from determinations of the density of each solution. The pycnometer, whose volume was about 20 cc., was filled three times with the given solution, thus three separate density determinations were made for each solution. Weights of cadmium iodide required to make 100 cc. of 0.5 *N* and 0.2 *N* solution were taken for each alcohol. In every case there was expansion as is shown in Table III.

TABLE III.

Solvent.	Conc.	Expansion per 100 cc. of solvent.	Solvent.	Conc.	Expansion per 100 cc. of solvent.
Ethyl alcohol.....	0.5 <i>N</i>	1.38 cc.	Methyl alcohol.....	0.5 <i>N</i>	1.10 cc.
	0.2 <i>N</i>	0.46 cc.		0.2 <i>N</i>	0.33 cc.

Thus it is seen that any error introduced into the calculation because of volume changes would alter all the results in the same direction and hence cannot in any way explain the great differences observed in the values for the specific refraction of these solutions.

The fact that the variations in the specific refraction of these two classes of solutions run parallel to the variations in the conductance curves for the same solutions indicates clearly a close relationship between conductance and specific refraction.

Summary.

(1) The conductance of methyl and ethyl alcoholic solutions of cadmium iodide at 25° has been measured and found to be in certain respects abnormal.

(2) These abnormalities have been shown to be similar to those previously observed in certain nonaqueous solutions of silver nitrate and a similar explanation has been assumed.

(3) The densities and refractive indices of these solutions have been measured at 20.5° and it has been shown that each is a rectilinear function of the concentration.

(4) The specific refraction calculated by the Lorentz-Lorenz formula has revealed certain abnormalities.

(5) A close connection has been pointed out between conductance and specific refraction.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

ATOMIC WEIGHT OF CADMIUM.

BY G. A. HULETT AND E. L. QUINN

Received May 13, 1915.

In an article on the atomic weight of cadmium, Baxter and Hartman¹ obtained the value 112.417 and call attention to the disagreement between this result and that obtained by Perdue and Hulett², Laird and Hulett,³ and Quinn and Hulett,⁴ where the value 112.3 was obtained by three independent methods.

Baxter and Hartman have pointed out some possible sources of error in our work which we think should receive some attention. In the last article we analyzed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode. This was done in order to avoid the inclusions which are always present in electrolytic deposits and very pronounced in the case of cadmium—we have found as much as 0.085%—but when the metal was dissolved in a mercury cathode, there were no inclusions.

Baxter and Hartman have also analyzed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode which was in a glass cell with a sealed-in platinum anode. These workers were unable to obtain all of the cadmium in a weighable form in their cell, and so made a correction for the cadmium in the electrolyte and wash-waters. Therefore, they suspected that we overlooked cadmium in our electrolyte and wash-water. We concentrated our electrolyte and wash-water to a small volume, but were unable to find cadmium, but Baxter and Hartman make the objection that we must have had a strong acid solution in our test. This, however, was not the case, as we evaporated the electrolyte and wash-waters in a platinum dish and heated until the fumes of sulfuric acid ceased; the residue was then taken up with a very little water and tested in a volume of 1 cc. with hydrogen sulfide. Comparisons were made with known amounts of cadmium in the same volume. There may, however, have been a trace of acid in our tests, as we did not endeavor to expel the last trace of acid. So some special tests have been made by one of us (Quinn), in regard to this point. A volume of liquid equal to the electrolyte and wash-water and containing 1½ cc. of strong sulfuric acid was evaporated with known amounts of cadmium sulfate, and the acid expelled just as in our previous work. The following amounts were taken:

1. 0.0002; 2. 0.0001; 3. 0.00005; 4. 0.00001 g. of cadmium.

¹ THIS JOURNAL, 37, 113.

² *J. Phys. Chem.*, 15, 1579.

³ *Trans. Am. Electrochem. Soc.*, 22, 385.

⁴ *J. Phys. Chem.*, 17, 780.

The first three tests showed cadmium at once, and smaller amounts in time. In addition to this, some tests were made with known amounts of acid present. On using an 18% solution of sulfuric acid with known amounts of cadmium, as follows:

1. 0.00007; 2. 0.00006; 3. 0.00005; 4. 0.00004 cadmium in 1 cc. acid.

The first three were detected at once, by the aid of hydrogen sulfide and smaller amounts in time. We conclude, therefore, that we could not have overlooked a weighable amount of cadmium in our experiments. We weighed from 4 to 6.5 g. of cadmium in analyzing the cadmium chloride so there could not have been a loss greater than one part in 100,000 due to this cause.

Baxter and Hartman used a glass cell with a mercury cathode for decomposing their cadmium chloride, and always found cadmium in their electrolyte and wash-water; this corresponds with our earlier experience in using this kind of a cell, and is the reason for developing the cell we finally used. Our observation was, that the difficulty was not inability to deposit all the cadmium in the mercury, but rather in the subsequent manipulations due to removing the layer of electrolyte which is always found between a mercury cathode and the glass part of a cell. In order to remove this layer of electrolyte and satisfactorily wash the amalgam it must be disturbed and there is danger not only of oxidation but also of loss of finely divided amalgam. We found that this could be avoided by using a platinum cup amalgamated internally, so that the mercury cathode wet the cup and it was therefore impossible for either electrolyte or water to get underneath the mercury. It was only necessary to wash the upper surface of the amalgam which was not disturbed during the process. The amalgam and cup were strongly cathode during the process of replacing the electrolyte with water. The final wash-water was removed with a pipet so that only a drop or two remained on the surface. Then the cup and amalgam were placed in a vacuum desiccator over a dehydrating agent, where the last traces of water rapidly disappeared and there was no layer of water between the amalgam and cup to cause spurting. We took precaution to avoid any loss of mercury by evaporation, and convinced ourselves that the method was reliable by means of blank tests as follows: We started with weighed pieces of our purest cadmium, dissolved these in hydrochloric acid, changed them to the sulfate, electrolyzed in our cell, and weighed the cadmium in the mercury cathode, following every detail of the manipulation used in analyzing the cadmium chloride. Five such tests were carried out. Two showed a gain, and three a loss, the probable error of a single determination was ± 0.00004 g., so that our method of determining cadmium in cadmium chloride gave us results which we think can be relied upon to two or three parts in 100,000, and we conclude that the percentage of cadmium in the

cadmium chloride we had was 61.217, with a probable error of not over two in the last decimal place. We question whether any method of analysis has been tested as rigidly as we have tested the method we used.

In our preliminary work we were unable to fuse cadmium chloride in a platinum tube in an atmosphere of hydrochloric acid gas without a measurable loss of platinum. But we found that with proper precautions this operation could be carried out in a quartz tube. Baxter and Hartman called attention to this part of our work and concluded from a loss in one of our experiments of 2.9 mg. of platinum that we probably had air (oxygen) in our hydrochloric acid gas. We were using a Smith crucible with a much larger surface than an ordinary platinum boat, but aside from this the statements of Baxter and Hartman are quite misleading. They took the value 2.9 from a table recording five experiments. The losses were from 2.9 to 0.6 mg. of platinum. The loss with new platinum was large but decreased with use. This is ten times as large as the figures given in Baxter and Hartman's paper. In our method of preparing the hydrochloric acid we took precaution to exclude air, all of the joints of the apparatus were glass or glass sealed, and that it was gas tight when evacuated was proven in each case. In fusing the cadmium chloride in a quartz tube we found no measurable loss in the weight of the tube.

In the work of Laird and Hulett¹ a cadmium coulometer was developed which used a mercury cathode in an amalgamated platinum cup. There could be no inclusions in the cadmium deposited in mercury, while the washing and handling of the amalgam had the advantages of avoiding the presence of the electrolyte between the mercury cathode and the cup. This coulometer was used in series with a silver coulometer and the cadmium and silver deposited by the same current showed a value of 112.31 as the atomic weight of cadmium if we take the accepted value for silver. Baxter and Hartman remark that it is not easy to obtain a coulometer silver deposit in which the proportion of inclusions is known. We must make decided exception to this statement, as this work was done in connection with an extended investigation of the inclusions in electrolytic silver. We developed a direct method for determining these inclusions and in the silver coulometer as used by us at that time the inclusions were 4.6 parts in 100,000 with a probable variation of about 0.5 part. Furthermore we made allowance for the inclusions in our electrolytic silver as stated in the article referred to by Baxter and Hartman. This question of inclusions in electrolytic silver is one which we will take up in detail later, although it is too small to be of significance as far as the atomic weight of cadmium is concerned.

The first work done by us² after we had developed our method of de-

¹ *Trans. Am. Electrochem. Soc.*, 22, 385.

² *Perdue and Hulett, J. Phys. Chem.*, 15, 1579.

termining cadmium deposited in mercury, was an analysis of cadmium sulfate crystals. Cadmium sulfate crystallizes with $8/3$ molecules of water and forms most remarkably perfect and clear crystals. The salt is not isomorphous with other substances and so offers an exceptional method of purifying the substance. The crystals are water-clear and do not show inclusions under highest magnification. They are very stable crystals, neither seeming to effloresce nor deliquesce in ordinary dry air. We observed the weight of a large crystal (5 g.) for a period of several weeks and found no measurable change in weight, although we could have detected 0.01–0.02 mg. The crystal remained in the balance case during this period. This seemed remarkable at first, but it is quite possible that a perfectly pure hydrated salt may not have a definite vapor pressure. This would follow from the phase rule; if we had only vapor and $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ there would be two phases and two components, so it would require the presence of another hydrate or the anhydrous salt for equilibrium. In other words, we would not necessarily be restricted to a particular pressure for a given temperature; in fact the salt appeared to us to behave much like a supercooled liquid. Various samples of this carefully crystallized salt were analyzed by depositing the cadmium in the mercury cathode as described above. The results were very concordant and gave the value 112.3. We did not place much reliance on this value as the determination of atomic weight by using a hydrated salt is of course questionable. Professor Richards¹ has pointed out that there are always inclusions of mother liquor in crystals, also he suggested the possibility of the solubility of water in these crystals. Both of these things are of course possible, but as far as the inclusion of electrolyte is concerned it was impossible to detect its presence by the use of a microscope; furthermore it might be pointed out that cadmium sulfate is a very soluble salt and the percentage of water in the saturated solution is not much over twice that in the crystals so that it would require inclusions amounting to one part in five hundred to affect the atomic weight of cadmium by as much as the amount in question. It is of course possible that there is a certain solubility of water in these crystals, since we must assume that every substance is soluble in every other substance, and there may have been a distribution of water between the solution and the crystals which would tend to give too small a percentage to the cadmium in the crystals. But this argument will also work in the other direction, since we must admit that the solute is also soluble in the crystals, and this would tend to give too great a percentage of cadmium in the crystals. There is, however, no definite information on these points and so we merely regard the analysis of the crystals as interesting.

PRINCETON, N. J.

¹ THIS JOURNAL, 33, 888 (1911).

THE SOLUBILITY-PRODUCT CONSTANT OF CALCIUM AND MAGNESIUM CARBONATES.

By JOHN JOHNSTON.

Received June 17, 1915.

In connection with certain calculations undertaken primarily to ascertain what degree of purity of magnesium carbonate might be expected if it were deposited by evaporation at constant temperature, of a solution containing both magnesium and calcium carbonates, it became necessary to determine the appropriate solubility-product constants.¹ Values of these quantities were calculated some years ago by Bodländer,² but these must now be revised because some of the constants employed by him are now known to be erroneous. Bodländer's calculations for calcium carbonate were revised later by Stieglitz,³ in connection with calculations relative to the effect of a change in the amount of carbon dioxide in the atmosphere upon the proportion of calcium carbonate in gypsum deposited by the evaporation at constant temperature of solutions (e. g., sea water) containing both. The available data have now all been recomputed so as to obtain really comparable values of these solubility-product constants which should be consonant with present-day knowledge of the various quantities involved in the calculations. With a knowledge of these constants one can make certain deductions which are important in relation to the question of the nature and character of the solid deposited when solutions containing both carbonates are evaporated down.

The constant cannot be obtained directly from observations on the solubility of the carbonate MCO_3 in pure water for two reasons: (1) because of the hydrolysis, the amount of which is in the first instance unknown; (2) because, as will be shown later, there cannot be true equilibrium except the solution be in contact, and have come to equilibrium, with a definite partial pressure of CO_2 which must be measured. But if the partial pressure of CO_2 is known, and the concentration of the saturated solution in contact with it (and with a definite solid phase) is determined, the solubility-product constant can readily be calculated. The equilibrium between the solid carbonate MCO_3 , the solution, and an atmos-

¹ For a thorough discussion of this quantity see a series of 7 papers entitled "The Effect of Salts on the Solubility of Other Salts," by A. A. Noyes, W. C. Bray, W. D. Harkins, and others, *THIS JOURNAL*, 33, 1643-86, 1807-73 (1911).

² Bodländer, *Z. physik. Chem.*, 35, 23 (1900).

³ Stieglitz, "The Relations of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulphate, Calcium Carbonate, and Calcium Bicarbonate in Water Solutions in Contact with it." In "The Tidal and Other Problems" by T. C. Chamberlin *et al.*, Carnegie Inst. Publ. No. 107 (1909). This paper is not so widely known as it deserves to be, probably because no one would look in such a book for a paper dealing with such a topic.

phere in which the partial pressure of CO_2 is P , is determined completely by the following four equations, in all of which, and throughout this paper, symbols such as $[M]$ represent the molar concentration of the species denoted by the symbol enclosed within the brackets:

- $$\begin{aligned} \text{(I). } & [M^{++}][\text{CO}_3^{--}] = K_M \\ \text{(II). } & [\text{H}_2\text{CO}_3] = k'[\text{CO}_2] = c'P \\ \text{(III). } & \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = k_1 \\ \text{(IV). } & \frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} = k_2 \end{aligned}$$

(I) defines the solubility product K_M , which we wish to calculate; (II) expresses the equilibrium between the undissociated dissolved carbonic acid and the partial pressure P of the CO_2 in contact with the solution; while (III) and (IV) define, respectively, the first and second ionization constants of carbonic acid in aqueous solution. At a given temperature the values of k_1 and k_2 , which are invariable, are known; the quantity c' , which is a measure of the solubility of CO_2 in the solution, varies, however, with the salt concentration of the solution. We shall now proceed to evaluate these constants.

The Solubility of CO_2 in Water and Salt Solutions.

The absorption-coefficient α of a gas, as given in tables of constants, is defined as the ratio of the volume of the gas dissolved (reduced always to 0°) to the volume of the water;¹ this ratio is, in accordance with Henry's law, independent of the pressure so long as the latter is not too high.

The molar concentration of the dissolved gas is then $\frac{\alpha P}{22.4}$, when P is expressed in atmospheres; for $\alpha/22.4$ we shall write c .

Now if we say that the concentration of un-ionized carbonic acid $[\text{H}_2\text{CO}_3] = cP$, we make the tacit assumption that none of the CO_2 exists as such in the solution, that all of it—apart from the ions—is present as the hydrate H_2CO_3 . But, strictly speaking, the H_2CO_3 (which, of course, is also in equilibrium with its ionization products) is in equilibrium with the CO_2 existing as such in solution and this in turn with the CO_2 in the gas phase; *i. e.*, if n is the proportion of the total CO_2 in solution existing as H_2CO_3 , $[\text{H}_2\text{CO}_3]/[\text{CO}_2]_s = n/(1-n)$, and $[\text{CO}_2]_s = m[\text{CO}_2]$. On the other hand, as actually measured,

$$c_1 = \frac{[\text{H}_2\text{CO}_3] + [\text{CO}_2]_s}{[\text{CO}_2]} \text{ and therefore, from the above, } c_1 = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} \frac{1}{n}.$$

¹ Some authors give the *solubility* of the gas, which is the actual volume of gas at the temperature in question absorbed by one volume of water; care must be taken to distinguish these two quantities.

The value of n is not known, but Walker and Cormack¹ from a discussion of the matter, conclude that at 18° it is almost certainly greater than 0.5. We shall therefore write

$$(V). [H_2CO_3] = nk [CO_2] = ncP$$

where $c = \alpha/22.4$, and n , the proportion of the total CO_2 in solution existing as H_2CO_3 , is greater than 0.5; we retain it, though it is unknown, in order to bring out the fact that the absolute value of certain of our constants depends upon the value assigned to n .

The absorption of CO_2 by water and aqueous solutions has been studied by several investigators with results which are satisfactorily concordant. Bohr² determined it in water and in two solutions of NaCl—respectively 1.17 and 3.44 N —at temperatures ranging up to about 60°; Geffcken³ made measurements at 15° and 25° of the solubility in 0.5 and 1.0 N solutions of a few salts and common acids. The change of absorption-coefficient is nearly proportional to the salt concentration, and varies relatively little from one salt to another. It is more nearly linear, and varies less for the several salts, when it is plotted against the ion-concentration of the solutions—as indeed we should expect since the proportion of un-ionized salt is small; but the existing data are too scanty to admit of any very strict generalization of this character. In the present work it was assumed that the absorption-coefficient of CO_2 in the carbonate solutions is the same as in sodium chloride of the same *equivalent* concentration; this mode of calculation leads to practically the same result as calculation on the basis of equality of absorption in solutions of equal ion-concentration, and is simpler to carry out. The coefficients actually used are given in the appropriate place; they were read from curves drawn on the basis of values interpolated from a large scale plot of Bohr's results in water and solutions of NaCl, as follows:

VALUES OF $c = \alpha/22.4$, WHERE α IS THE ABSORPTION COEFFICIENT OF CO_2 .

Temperature.	In water.	In 1.17 N solution.	In 3.44 N solution.
3.5	0.0672	0.0484	0.0270
12	0.0500	0.0367	0.0213
16	0.0441	0.0328	0.0193
25	0.0338	0.0260	0.0159
30	0.0297	0.0232	0.0142
40	0.0236	0.0185	0.0117

The next step is to obtain the value of k_1 and k_2 , or more particularly of the ratio k_1/k_2 , which is obtained directly from McCoy's⁴ work on the carbonate-bicarbonate equilibrium.

¹ Walker and Cormack, *J. Chem. Soc.*, 77, 13-14 (1900); see also Walker, *Ibid.*, 82, 182 (1903).

² C. Bohr, *Ann. Physik*, 68, 500 (1899).

³ G. Geffcken, *Z. physik. Chem.*, 49, 257 (1904).

⁴ H. N. McCoy, *Am. Chem. J.*, 29, 437 (1903).

The Carbonate-Bicarbonate Equilibrium.

On dividing Equation III by Equation IV we obtain

$$(VI). \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{--}][\text{H}_2\text{CO}_3]} = \frac{k_1}{k_2} = r,$$

r being the ratio of the first to the second ionization constant of H_2CO_3 ; whence by combination with V

$$(VII). \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{--}]cP} = nr.$$

By means of Equation VII values of nr can be calculated from McCoy's data on the equilibrium at 25° between sodium bicarbonate and carbonate in aqueous solutions in contact with a measured partial pressure (P) of CO_2 . Such calculations were made by McCoy; in the present calculation corrections which were indicated by McCoy, but not carried out, have been made for the change of solubility of CO_2 in salt solutions and for the degree of ionization of the salts.¹ The latter correction was made on the basis of the principle, now well established,² that the degree of ionization of a salt in a mixture is sensibly equal to that of a salt of the same valence type at the same total ion-concentration; this is, at the least, a more accurate procedure than the direct calculation from the conductivity of solutions of sodium carbonate or bicarbonate, on account of the complexity of the solutions and the consequent difficulty of interpreting the results.

McCoy made three series of determinations, all at 25° , the results of which are reproduced in Table I; in these three series the total concentration of sodium was, respectively, 0.1, 0.3 and 1.0 N . The values of c (the molar absorption of CO_2) and of γ_1 and γ_2 (the degrees of ionization of NaHCO_3 and Na_2CO_3 , respectively) which were adopted follow:

	Total conc. of Na.	c .	γ_1 .	γ_2 .
A.....	0.1	0.0323	0.81	0.70
B.....	0.3	0.0295	0.76	0.63
C.....	1.0	0.0233	0.65	0.56

It will be observed that the values of nr , which are very satisfactorily concordant in each series, decrease with increasing concentration; this decrease, which is too large to be due to simple errors in the values of c and γ adopted, may be attributed to failure of the tacit assumptions that n and the activity of the water are constant.³ However this may

¹ Cf. Stieglitz, *Carnegie Inst. Publ.*, 107, 243-5 (1909).

² See, for instance, publications from the laboratory of A. A. Noyes.

³ It may be noted that if we assume the relative decrease of solubility of CO_2 with increase of salt concentration to be a rough measure of the decrease in activity of the water (as has been done in attempts to estimate the extent of hydration), and calculate on this basis, the three mean values of nr become 5500, 5350 and 5000, respectively.

be, we shall adopt here the value of 5600, which is the extrapolated value at zero concentration when the three above results are plotted; in other words, $5600 = nk_1/k_2$ where k_1 and k_2 are the first and second ionization-constants of H_2CO_3 .

TABLE I.—VALUES OF $n\tau = \frac{[HCO_3^-]^2}{[CO_3^{=}]cP''}$ CALCULATED FROM MCCOY'S DATA ON THE

CARBONATE-BICARBONATE EQUILIBRIUM AT 25°.

P. (Atm.)	Conc. of total bicarbonate. x.	$[HCO_3^-]$ = $\gamma_1 x$.	Conc. of total carbonate. y.	$[CO_3^{=}]$ = $1/\gamma_2 y$.	$n\tau$.
A: $x + y = 0.1$.					
0.00161	0.0682	0.0552	0.0318	0.0111	5260
0.00159	0.0690	0.0559	0.0310	0.0109	5600
0.00259	0.0760	0.0615	0.0240	0.0084	5380
0.00294	0.0775	0.0628	0.0225	0.0079	5300
0.00322	0.0781	0.0633	0.0219	0.0077	5040
0.00404	0.0818	0.0662	0.0182	0.0064	5300
0.0223	0.0951	0.0770	0.0049	0.0017	4840 ¹
0.0749	0.0985	0.0798	0.0015	0.0005	5260 ¹
					5300
B: $x + y = 0.3$.					
0.00319	0.1737	0.132	0.1263	0.0398	4650
0.00583	0.2037	0.155	0.0963	0.0303	4610
0.01044	0.2307	0.176	0.0693	0.0218	4610
0.0	0.2556	0.194	0.0444	0.0140	4400
0.0	0.2664	0.203	0.0336	0.0106	4770
0.0	0.2778	0.211	0.0222	0.0070	4780
					4650
C: $x + y = 1.0$.					
0.0436	0.758	0.492	0.242	0.0678	3510
0.0624	0.810	0.526	0.190	0.0533	3570
0.1021	0.860	0.559	0.140	0.0392	3350
0.1682	0.902	0.586	0.098	0.0274	3200
					3450

Walker and Cormack,² from concordant determinations of the conductivity of solutions of carbonic acid, concluded that at 18°

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3] + [CO_2]_s} = 3.04 \times 10^{-7}$$

whence

$$k_1 = \frac{3.04 \times 10^{-7}}{n} \text{ at } 18^\circ \quad \text{or} \quad \frac{3.4 \times 10^{-7}}{n} \text{ at } 25^\circ$$

¹ Omitted in taking the mean because of the small percentage accuracy of $[CO_3^{=}]$ in those cases.

² Walker and Cormack, *J. Chem. Soc.*, 77, 8 (1900).

³ This value is derived from that at 18° by means of the van't Hoff formula on the basis that the heat change accompanying the reaction is 2700 cal. (Lewis and Randall, *This Journal*, 37, 467 (1915).)

where n , as before, is the fractional amount of the total CO_2 in solution existing in the form of H_2CO_3 . Consequently

$$k_2 = \frac{k_1}{r} = \frac{3.4 \times 10^{-7}}{n} \cdot \frac{n}{5600} = 6 \times 10^{-11}$$

which is identical with the result originally computed by McCoy (6.0×10^{-11}), with that (6.4×10^{-11}) recalculated from the work of Shields¹ on the hydrolysis of sodium carbonate, and with that obtained by Auerbach and Pick² (6×10^{-11} at 18°) using still other methods.

The above value of nr was determined for a temperature of 25° , but it may be applied with safety at other temperatures not too far removed from 25° ; in using this value for other temperatures we are tacitly assuming that nr remains constant—an assumption which, though it may well prove to be far from correct, is the best that can be done so long as the necessary data are unknown.

The Solubility-Product Constant.

On substituting in Equation VII for $[\text{CO}_3^{=}]$ its value from Equation I we obtain finally

$$[M^{++}][\text{HCO}_3^-]^2 = nrK_M cP$$

or

$$(VIII). \quad nrK_M = \frac{[M^{++}][\text{HCO}_3^-]^2}{cP}.$$

Thus the solubility-product constant K_M of a carbonate can be calculated if corresponding values of the quantities on the right hand side of Equation VIII are known; the factors in the numerator can be derived from measurements of the solubility of the carbonate MCO_3 in presence of CO_2 at the pressure P by (1) correcting for the (always small and frequently negligible) amount of neutral carbonate present,³ (2) multiplying the concentration of bicarbonate so obtained by the appropriate value of the degree of ionization, (3) inserting the appropriate values of c and P , and working out. We shall now proceed to some actual cases; but before doing so, we wish to point out that the solubility-product constant (like the solubility itself) has no significance except in relation to a definite solid phase—that this quantity is not the same for the three known forms of CaCO_3 (calcite, aragonite, vaterite) nor again for $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$,

¹ Shields, *Z. physik. Chem.*, 12, 167 (1893).

² Auerbach and Pick, "Die Alkalität wässriger Lösungen kohlensaurer Salze," *Arbeiten kais. Gesundheitsamt.*, 38, 243 (1911).

³ As will be evident later, it is not admissible to subtract (as Bodländer did in the case of MgCO_3) a constant quantity corresponding to the saturation concentration of the neutral carbonate as measured in pure water; the latter, moreover, is not a definite quantity, for there can be no equilibrium except in presence of a definite pressure of CO_2 .

$\text{MgCO}_3 \cdot \text{H}_2\text{O}$ and MgCO_3 except at the transition point of one form to the other.

The Solubility-Product Constant of Calcium Carbonate (Calcite).

In this case there is no doubt as to the nature of the solid phase. Determinations of the solubility of CaCO_3 at 16° have been made by Schloesing¹ at partial pressures of CO_2 ranging up to 1 atm. and by Engel² at pressures from 1 to 6 atm. Calculations based on their results are presented in Tables II and III.

The first two columns of Table II contain the actual measurements of the partial pressure (P , in atm.) and the total concentration of calcium in the solution (expressed in mols per liter); the quantities in the other columns are derived from these, except that the values of the degree of ionization (γ) in the fourth column are those (as derived from the conductivity) of equivalent solutions of calcium acetate. In the third column are given the corrected total concentrations of bicarbonate, from which, by multiplication with the appropriate value of γ , the values of $[\text{HCO}_3^-]/2$ tabulated in the fifth column were obtained; the sixth column gives the total concentration of calcium ion, which $= \frac{1}{2}[\text{HCO}_3^-] + [\text{CO}_3^{--}]$, and in the last are the computed values of the constant πK_{Ca} .

TABLE II.—CALCULATIONS ON THE BASIS OF SCHLOESING'S DATA ON THE SOLUBILITY OF CALCITE IN WATER CONTAINING cP MOLS CO_2 AT 16° ; $c = 0.0441$.

P . (Atm.)	Total [Ca]. Mols l.	Total $\text{Ca}(\text{HCO}_3)_2$. Mols l.	γ .	$\frac{1}{2}[\text{HCO}_3^-]$.	$[\text{Ca}^{++}]$.	πK_{Ca} .
0.000504	0.000746	0.000731	0.906	0.000663	0.000678	5.36×10^{-8}
0.000808	0.000850	0.000837	0.904	0.000757	0.000770	4.95
0.00333	0.001372	0.001364	0.890	0.001214	0.001222	4.99
0.01387	0.002231	0.002226	0.870	0.001940	0.001945	4.79
0.02820	0.002965	0.002961	0.856	0.002537	0.002541	5.28
0.05008	0.003600	0.003597	0.844	0.003045	0.003048	5.10
0.1422	0.005330	0.005328	0.822	0.00438	0.00438	5.36
0.2538	0.006634	0.006632	0.811	0.00538	0.00538	5.57
0.4167	0.007875	0.007874	0.798	0.00628	0.00628	5.39
0.5533	0.008855	0.008854	0.790	0.00699	0.00699	5.60
0.7297	0.00972	0.00972	0.785	0.00763	0.00763	5.52
0.9841	0.01086	0.01086	0.778	0.00845	0.00845	5.56

5.30×10^{-8}

TABLE III.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF CALCITE IN WATER CONTAINING cP MOLS CO_2 AT 16° .

P . (Atm.)	Total [Ca]. Mols l.	c .	γ .	$[\text{Ca}^{++}] = \frac{1}{2}[\text{HCO}_3^-]$.	πK_{Ca} .
1	0.01085	0.0439	0.778	0.00844	5.48×10^{-8}
2	0.01411	0.0438	0.756	0.01066	5.53
4	0.01834	0.0437	0.730	0.01338	5.48
6	0.02139	0.0437	0.713	0.01525	5.41

5.47×10^{-8}

¹ Schloesing, *Compt. rend.*, 74, 1552; 75, 70 (1872).

² Engel, *Ann. chim. phys.*, [6] 13, 348 (1888).

A word is necessary as to the method of correcting for the neutral carbonate present—the correction namely ($= [\text{CO}_3^{=}]$), applied in deriving the numbers in the third column from those in the second. From Equation VII $[\text{HCO}_3^{-}]/[\text{CO}_3^{=}] = nrcP = 247P$ at 16° ; and consequently if an approximate value of $[\text{HCO}_3^{+}]$ is known in advance, the concentration of $[\text{CO}_3^{=}]$ (which relatively is always small) can be estimated. Thus in the most dilute solution (where the correction is greatest) of Table II, the correction is $(0.00134)^2/247 \times 0.0005 = 0.000015$.¹ It can also be obtained directly as soon as a rough value of the solubility-product constant $[\text{Ca}^{++}][\text{CO}_3^{=}]$ is ascertained. The amount of this correction in all the solutions is evident by subtracting the figures in Column 3 (or 5) from those in Column 2 (or 6); in the stronger solutions it is obviously entirely negligible.

Table III is identical in arrangement with Table II, except that the relative absorption-coefficients of CO_2 are given in the third column; in this case the correction for neutral carbonate is entirely negligible, so that the total concentrations of bicarbonate are identical with the experimentally determined concentrations in the second column.

The constancy of the values tabulated in the last column is surprisingly good, especially in view of the fact that P ranges from 0.0005 atm. (slightly greater than the amount ordinarily present in the air) to 6 atm.; in other words, the product remains constant even when the concentration of one of the factors in the equilibrium changes as much as ten thousandfold. The mean value derived from the stronger solutions (where the experimental accuracy is greatest) is 5.50×10^{-8} , a value from which we can calculate with confidence the solubility of calcite in water at 16° saturated with CO_2 at any pressure up to that at which calcium bicarbonate would begin to appear as solid phase at this temperature. Accordingly the solubility-product constant of calcite at 16° is

$$[\text{Ca}^{++}][\text{CO}_3^{=}] = K_{\text{Ca}} = \frac{5.50 \times 10^{-8}}{5600} = 0.98 \times 10^{-8}. \text{ It is of little use}$$

to compare this with the "solubility in pure water"² because, except there be no vapor phase, the latter is meaningless except in relation to a definite partial pressure of CO_2 ;³ for a definite concentration of CO_2 , in accordance with Equations VI and VII, can exist in equilibrium only with definite

¹ This is just about 9% of the quantity which has been considered to represent the solubility of CaCO_3 in pure water. From this correction the extent of hydrolysis in the several solutions can obviously be readily calculated.

² The most recent determinations of this quantity are by Kendall (*Phil. Mag.*, 23, 957 (1912)), who found at 25° , 50° and 100° , respectively, 14.3, 15.0 and 17.8 mg. CaCO_3 per liter. There is of course no assurance that the partial pressure of CO_2 was actually the same at all temperatures, so that these values are not necessarily even comparable with one another.

³ See Table IV., *postea*.

concentrations of HCO_3^- and H_2CO_3 , and the latter in turn requires a definite partial pressure of CO_2 .¹

Determinations of the amount of CaCO_3 in solution in presence of CO_2 have also been made by others. Treadwell and Reuter² made very painstaking analyses of a series of such solutions at 15° , but—as is obvious from a perusal of their mode of working—did not secure equilibrium conditions, a fact which is borne out by the lack of constancy of the calculated solubility-product constant. Quite recently Leather and Sen³ made series of determinations at a number of temperatures between 15° and 40° ; their solutions may have attained equilibrium, but their mode of analysis is unsatisfactory.⁴ This was confirmed by the calculations, which yielded very irregular results; the most that one can deduce from them is that the solubility-product constant of calcite probably decreases somewhat with the temperature, becoming apparently about 0.5×10^{-8} at 40° .

Seyler and Lloyd⁵ have also made a series of determinations of the equilibrium between solid calcium carbonate and water and certain dilute salt solutions containing excess of carbon dioxide; they kept the solutions, which were shaken occasionally, for long periods in stoppered bottles completely filled with liquid, and ascertained by titration the concentration of free CO_2 and of the dissolved carbonate. Unfortunately, however, their experiments were carried out at “the temperature of the laboratory;” nevertheless despite this indefiniteness, it seemed worth while to include their results (which have been recalculated so as to conform with the others presented in this paper) because these demonstrate that the solubility-product constant of calcite is not affected by the presence in the solution of small excess amounts of added Ca^{++} (as CaCl_2 or CaSO_4) or HCO_3^- (as NaHCO_3). In this case $nK_{\text{Ca}} = [\text{Ca}^{++}][\text{HCO}_3^-]^2/[\text{H}_2\text{CO}_3]$, where $[\text{H}_2\text{CO}_3]$ is the concentration of free CO_2 in solution as determined by titration; as is evident from the table its value varies about a mean, the general average being 4.80×10^{-5} . Consequently $K_{\text{Ca}} = \frac{4.80 \times 10^{-5}}{5600} = 0.86 \times 10^{-8}$ at the “temperature of the

¹ Similar remarks with respect to the equilibrium between sodium carbonate and bicarbonate were made by McCoy (*Am. Chem. J.*, 29, 456ff. (1903)).

² Treadwell and Reuter, *Z. anorg. Chem.*, 17, 170 (1898).

³ Leather and Sen, *Memoirs Dept. Agric. India*, Chem. Series, 1, No. 7 (1909).

⁴ One obvious error is a loss of CO_2 , because in some cases especially in similar work with MgCO_3 (see *postea*), the total CO_2 in solution, as given in their tables, is insufficient to convert all of the base present to bicarbonate. As McCoy notes (*Am. Chem. J.*, 29, 444 (1903)) “Carbon dioxide may readily be lost from solutions rich in bicarbonate, if care be not taken to render them alkaline at once. Low results were invariably obtained when the bicarbonate solutions were measured into beakers and allowed to stand, even for four or five minutes, before adding an excess of alkali.”

⁵ Seyler and Lloyd, *J. Chem. Soc.*, 95, 1347 (1909).

laboratory," whence one might deduce that this temperature was about 20°. Seyler and Lloyd also investigated the effect of the presence of a small amount of a salt (NaCl , Na_2SO_4 , MgSO_4) containing no ion in common with calcium carbonate, and found an increase in the total calcium in solution, in qualitative agreement with theory; by allowing for the undissociated fraction of the several salts present one could indeed calculate the solubility-product constant in these cases too, but such calculations would have little value by reason of the paucity and uncertainty of the experimental data.

TABLE IIIa.—CALCULATIONS ON THE BASIS OF THE RESULTS OF SEYLER AND LLOYD ON THE SOLUBILITY OF CALCITE IN WATER AND DILUTE SALT SOLUTIONS CONTAINING FREE CO_2 .

Free CO_2 [H_2CO_3].	[Ca] as bicarbon- ate.	Conc. of added salt. Mols l.	γ_1 .	γ_2 .	[Ca^{++}] from bicarbonate = $\frac{1}{2}[\text{HCO}_3^-]$.	[Ca^{++}] from added salt.	Total [Ca^{++}].	πK_{Ca} .
Without added salt.								
0.00269	0.00370	0.845	...	0.00313	0.00313	4.56 $\times 10^{-8}$
0.00362	0.00414	0.840	...	0.00348	0.00348	4.66
0.0100	0.00604	0.816	...	0.00492	0.00492	4.76
0.0114	0.00657	0.810	...	0.00532	0.00532	5.28
In presence of CaCl_2 .								
0.00395	0.00306	0.00625	0.788	0.788	0.00242	0.00493	0.00735	4.36
In presence of CaSO_4 .								
0.00104	0.00244	0.00119	0.848	0.665	0.00207	0.00079	0.00286	4.71
0.00181	0.00304	0.00119	0.838	0.647	0.00255	0.00077	0.00332	4.77
0.00206	0.00316	0.00119	0.837	0.644	0.00265	0.00077	0.00342	4.66
0.00315	0.00362	0.00119	0.831	0.633	0.00301	0.00076	0.00377	4.34
0.00455	0.00441	0.00119	0.821	0.615	0.00362	0.00073	0.00435	5.01
0.00656	0.00492	0.00119	0.815	0.605	0.00401	0.00072	0.00473	4.64
0.00356	0.00350	0.00312	0.832	0.636	0.00291	0.00198	0.00489	4.65
0.00494	0.00379	0.00625	0.829	0.629	0.00314	0.00394	0.00708	5.66
In presence of NaHCO_3 .								
0.00475	0.00278	0.00625	0.817	0.817	0.00227	0.00511 ¹	0.00965 ²	4.45
0.00406	0.00170	0.0125	0.798	0.798	0.00136	0.01000 ¹	0.01272 ²	5.42
General mean, 4.80 $\times 10^{-8}$								

A knowledge of these constants renders unnecessary experimental work such as that of Keiser and McMaster,³ who investigated the ratio of the excess of CO_2 in solution to the amount of CaCO_3 . And the fact of this constancy is sufficient reply to statements such as the following: "While there is some evidence which supports the view that calcium bicarbonate exists in the dissolved state, the observed facts can be regarded just as logically and more conveniently as the result of the specific solvent power of the carbon dioxide-water mixture."⁴

¹ [HCO_3^-] from added salt.

² Total [HCO_3^-].

³ Keiser and McMaster, *THIS JOURNAL*, 30, 1714 (1908).

⁴ Cameron and Robinson, *J. Physic. Chem.*, 12, 573 (1908).

The Solubility of Calcite in Water in Contact with the Atmosphere.

The amount of calcium carbonate which will dissolve in water in contact with the air, and the variation of this solubility with the CO_2 content of the air, are of very great importance in connection with a number of geological processes of very widespread occurrence. The saturated solution of calcite under these conditions is so dilute that the concentration of CO_3^{--} (and even of OH^-) is not negligible in summing up the total concentration of negative ions; consequently the calculations can be carried out only by a series of approximations. One has namely to determine values of $[\text{Ca}^{++}]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{--}]$ and $[\text{OH}^-]$, which shall simultaneously satisfy the condition

$$[\text{Ca}^{++}] = \frac{1}{2}[\text{HCO}_3^-] + [\text{CO}_3^{--}] + \frac{1}{2}[\text{OH}^-]$$

and three of the following equations:¹

- (I). $[\text{Ca}^{++}][\text{CO}_3^{--}] = K_{\text{Ca}} = 0.98 \times 10^{-8}$
- (VII). $[\text{HCO}_3^-]^2/[\text{CO}_3^{--}] = nrcP = 247 P$
- (VIII). $[\text{Ca}^{++}][\text{HCO}_3^-]^2 = nK_{\text{Ca}}cP = 2.425 \times 10^{-6} P$
- (IX). $[\text{OH}^-]/[\text{HCO}_3^-] = K_w/nk_1cP = 3.730 \times 10^{-7}/P$
- (X). $[\text{OH}^-]^2/[\text{CO}_3^{--}] = K_w^2/nk_1k_2cP = 3.435 \times 10^{-11}/P$

In order to obtain the total concentration of calcium in the solution from the ion-concentrations obtained in this way one must correct for the ionization of the $\text{Ca}(\text{HCO}_3)_2$,² this can be done by dividing the value of $\frac{1}{2}[\text{HCO}_3^-]$ by the appropriate fractional ionization (γ_1), the latter being read by inspection from a curve obtained by plotting the fractional ionization—as derived from the conductivity of solutions of calcium acetate—against the concentration of Ca^{++} . The results derived in this way for various partial pressures of CO_2 such as may occur in atmospheric air are presented in Table IV.

The amount of CO_2 in ordinary air, which is about 3 parts in 10,000, corresponds, on the basis of Table IV, to about 63 parts CaCO_3 per million; and, as is evident from the table, comparatively small changes in the concentration of CO_2 in the air may, in nature, easily bring about the solution or deposition of very large quantities of calcium carbonate. Its solubility would of course be slightly different in natural waters—springs, rivers or the sea; the presence of other calcium salts would make it smaller

¹ The numerical values refer to calcite at 16° , where $c = 0.0441$. Equation IX is obtained by combination of (III) and (V) with the relation $[\text{H}^+][\text{OH}^-] = K_w = 0.5 \times 10^{-14}$ at 18° ; (X) by combination of (VII) and (IX). It may be noted that, for the purpose of these approximations, the various equations must be absolutely consistent; hence it is necessary to retain a larger number of figures than is warranted by the accuracy of the several constants, until the final result is written down.

² The concentrations of CO_3^{--} and of OH^- are so small that ionization is practically complete.

by an amount readily calculable, while salts of other radicals would of themselves make it somewhat larger. It would lead too far to discuss satisfactorily this question here, and its bearing on a number of geologic phenomena.¹ It may be affirmed, however, on the basis of analyses cited by F. W. Clarke,² that many natural waters are substantially saturated with calcium carbonate; while it is certain that the surface layers of the larger part of the ocean, except possibly in the Arctic and Antarctic, must in general be substantially saturated.

TABLE IV.—THE CALCULATED SOLUBILITY OF CALCITE IN WATER AT 16° IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE P OF CO_2 .

P .	$[\text{Ca}^{++}]$.	$\frac{1}{2}[\text{HCO}_3^-]$.	η .	$[\text{Ca}]$ as $\text{Ca}(\text{HCO}_3)_2$.	$[\text{CO}_3^{--}]$.	$[\text{OH}^-]$.	Total $[\text{Ca}]$.	Parts CaCO_3 per million
0.00020	0.000509	0.000488	0.919	0.000532	0.000019	1.82×10^{-4}	0.000552	55
0.00025	0.000546	0.000527	0.917	0.000574	0.000018	1.57	0.000593	59
0.00030	0.000579	0.000561	0.915	0.000613	0.000017	1.40	0.000631	63
0.00035	0.000608	0.000591	0.914	0.000647	0.000016	1.26	0.000664	66
0.00040	0.000635	0.000618	0.913	0.000677	0.000016	1.15	0.000694	69
0.00045	0.000659	0.000643	0.912	0.000705	0.000015	1.07	0.000721	72
0.00050	0.000682	0.000666	0.912	0.000731	0.000014	1.00	0.000746	75

The concentration of OH^- , tabulated in the seventh column of Table IV, which is a measure of the alkalinity of the solutions, increases with diminishing partial pressure of CO_2 ; indeed purposive variation of the proportion of CO_2 over a solution in contact with excess of calcium carbonate might, in some instances, prove a convenient method of establishing and controlling a definite alkalinity in the solution. Such an action apparently goes on on a large scale continuously in the sea, the alkalinity of which corresponds closely to that of the saturated solution of CaCO_3 in equilibrium with air containing three parts CO_2 per 10,000.

The Solubility-Product Constant of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (Nesquehonite).

Determinations were made by Engel⁴ of the equilibrium between $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, water, and (a) CO_2 at pressures ranging up to 6 atm. at 12° and (b) CO_2 at 1 atm. at temperatures ranging up to 50°; the

¹ This will be treated in another paper now in preparation.

² F. W. Clarke, "Data of Geochemistry," U. S. Geological Survey, *Bull.* 59ff. (1911).

³ See Ruppin, "Die Alkalinität des Meerwassers," *Z. anorg. Chem.*, 66, 122-9 (1910), who gives numerous references.

⁴ Engel, *Ann. chim. phys.*, [6] 13, 353, 354 (1888). He also gives a series of preliminary results for pressures ranging up to 9 atm. at 19.5°, with "magnesium hydrous carbonate" as solid phase, which when calculated give quite a fair constant; these have not been included because the nature of the solid phase at equilibrium is doubtful.

⁵ Similar determinations have been published very recently by Leather and Sen (*Memoirs Dept. Agric. India*, Chem. Series, 3, No. 8 (1914); but—apart altogether from the circumstance that it is very questionable whether equilibrium was really attained in their experiments—their analytical results cannot be trusted, since the

form the basis for the figures presented in Tables V and VI. These tables are identical in arrangement with Table III, as the correction for $[\text{CO}_3^{--}]$ is absolutely negligible at the concentrations in question; the absorption-coefficient is that for solutions of sodium chloride of equivalent concentration at the particular temperature, the fractional ionization is that of an equivalent solution of magnesium chloride.¹

TABLE V.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ IN WATER CONTAINING cP MOLS CO_2 AT 12° .

P (Atm.)	Total [Mg]. Mols l.	α	Ionization γ	$[\text{Mg}^{++}] = [\text{HCO}_3^-]/2$	πK_{Mg}
0.5	0.255	0.0431	0.686	0.175	1.06
1	0.326	0.0418	0.680	0.222	1.05
1.5	0.379	0.0406	0.675	0.256	1.10
2	0.417	0.0399	0.672	0.280	1.10
2.5	0.443	0.0393	0.670	0.297	1.07
3	0.474	0.0388	0.669	0.317	1.09
4	0.519	0.0379	0.666	0.346	1.09
6	0.612	0.0362	0.662	0.404	1.19
					1.08

TABLE VI.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ IN WATER CONTAINING c MOLS CO_2 AT SEVERAL TEMPERATURES.

t.	Total [Mg]. Mols l.	α	γ	$[\text{Mg}^{++}] = [\text{HCO}_3^-]/2$	πK_{Mg} at t.
3.5	0.422	0.0525	0.672	0.283	1.73
12	0.326	0.0418	0.680	0.222	1.05
18	0.262	0.0363	0.686	0.180	0.64
22	0.237	0.0328	0.690	0.164	0.54
30	0.187	0.0273	0.700	0.131	0.33
40	0.140	0.0223	0.715	0.100	0.18
50	0.113	0.0186	0.725	0.082	0.12

From the last column of Table V it is evident that we have a very satisfactory constant, a constancy which is the more remarkable in view of the fact that the total ion-concentration of the solution is so large—above 0.5 M throughout. This constancy inclines one to the belief that the solubility-product constant will, when the experimental results can be properly interpreted, be found to hold for substances, the saturated solutions of which are not extremely dilute.² From the mean value the ratio of the total amount of CO_2 in the solution (as given by them) to the magnesia is very irregular and in many cases is even less than 2. (Cf. footnote 4, p. 2009.) Moreover, their results when plotted directly show great inconsistencies. In accordance with this the calculated values of the product πK_{Mg} are very irregular and show no approach to constancy.

¹ On the basis of its value at 18° in each case; but this introduces no appreciable error, since the variation in extent of ionization is very small at temperatures up to 50° . (See, for instance, Noyes and Johnston, THIS JOURNAL, 31, 987 (1909).)

² It may be added that the fact of this constancy is a criterion of the substantial accuracy of the γ values chosen; for a change of 3% in the values assigned to γ suffices

product $K_{Mg} = [Mg^{++}][CO_3^{--}] = \frac{1.08}{5600} = 1.93 \times 10^{-4}$ at 12° when the solid phase is $MgCO_3 \cdot 3H_2O$.¹

From the numbers in the last column of Table VI, the values of the solubility-product constant were calculated; these are reproduced in Table VII, alongside values calculated from an equation which was derived as follows: If we integrate the well-known equation $\ln K/dT = Q/RT^2$ on the basis that Q (the heat effect of the reaction considered) is constant over the temperature range, we obtain $\ln K = (-Q/RT) + C$, which has the form $\log K = (A/T) + B$; or, in other words, when values of $\log K$ are plotted against $1/T$, the graph is a straight line. The plot of the data proved to be a straight line, the equation to which is

$$(XI). \quad \log K = (2315/T) - 11.870.$$

The agreement between the values calculated directly and those derived from Equation XI is very good, all things considered. Moreover, by comparing the above equations, we can calculate Q —namely $Q = -2315 \times 2.303 R = -10600$ cal.; that is, the heat change corresponding to the reaction $MgCO_3 \cdot 3H_2O = Mg^{++} + CO_3^{--} + 3H_2O$ is an evolution of 10600 cal.

TABLE VII.—THE SOLUBILITY-PRODUCT CONSTANT OF $MgCO_3 \cdot 3H_2O$ AT VARIOUS TEMPERATURES.

t.	T.	$K_{Mg} = [Mg^{++}][CO_3^{--}]$	
		Derived from Table VI.	Calc. from Equation XI.
3.5	276.5	3.09×10^{-4}	3.17×10^{-4}
12	285	1.88	1.78
18	291	1.14	1.21
22	295	0.97	0.95
30	303	0.59	0.59
40	313	0.32	0.33
50	323	0.21	0.20

The Solubility of $MgCO_3 \cdot 3H_2O$ in Water in Contact with the Atmosphere, and the Question of Basic Magnesium Carbonates.—The figures in Table VII enable one to calculate, in precisely the same way as was to produce a pronounced trend in the values of nK_{Mg} . Conversely, careful work of this character could be used as a means of determining the extent of ionization, which would be practically independent of the assumptions made in the usual methods of deriving this quantity. To avoid misconception, it may be remarked that the values of γ as given in the table were all chosen before any of the calculations of the values of nK_{Mg} were made.

¹ The solubility of $MgCO_3 \cdot 3H_2O$ in "pure water" is given by Auerbach (*Z. Elektrochem.*, 10, 161 (1904)) as 0.0095 mol per liter at 15° , 0.0087 at 25° , and 0.0071 at 35° ; but these results are again indefinite for the reason already pointed out (p. 2008). In this case, as it happens, the process of hydrolysis goes on quite slowly at ordinary temperatures.

done for calcite, the total solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at temperatures up to 50° in water in contact with any partial pressure of CO_2 ; but in this case the sparing solubility of $\text{Mg}(\text{OH})_2$ introduces an added complication which enters whenever the partial pressure is reduced to a definite limiting value, the magnitude of which depends upon the temperature. In order to bring out this point, which has a very important bearing on the composition of basic carbonates of magnesia, we shall make the calculations for 18° and partial pressures ranging from 0.0002 to 0.0005 atm. One has again to determine values of $[\text{Mg}^{++}]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{--}]$ and $[\text{OH}^-]$ which shall satisfy the condition $[\text{Mg}^{++}] = \frac{1}{2}[\text{HCO}_3^-] + [\text{CO}_3^{--}] + \frac{1}{2}[\text{OH}^-]$, two of the following equations:¹

$$\text{(VII). } [\text{HCO}_3^-]^2/[\text{CO}_3^{--}] = nrcP = 229.6 P$$

$$\text{(VIII). } [\text{Mg}^{++}][\text{HCO}_3^-]^2 = nrK_{\text{Mg}}cP = 2.755 \times 10^{-2} P$$

$$\text{(IX). } [\text{OH}^-]/[\text{HCO}_3^-] = K_w/nk_1cP = 4.012 \times 10^{-7} P$$

$$\text{(X). } [\text{OH}^-]^2/[\text{CO}_3^{--}] = K_w^2/nk_1k_2cP = 3.694 \times 10^{-11}/P$$

and either (I). $[\text{Mg}^{++}][\text{CO}_3^{--}] = K_{\text{Mg}} = 1.2 \times 10^{-4}$

or (XII). $[\text{Mg}^{++}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$ ²

The choice between (I) and (XII) is not an arbitrary one, but depends upon the value of P . For by combination of Equations I and X (or VIII and IX), one obtains the relation

$$[\text{Mg}^{++}][\text{OH}^-]^2 = \frac{K_w^2 K_{\text{Mg}}}{nk_1k_2cP} = \frac{4.433 \times 10^{-15}}{P} \text{ at } 18^\circ,$$

a value which exceeds the product XII whenever P is less than 0.000369. Consequently, when P is less than 0.000369, the solid phase in equilibrium with the solution at 18° is not $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, but $\text{Mg}(\text{OH})_2$; in other words, this is a type of transition pressure, both solid phases being in equilibrium with the solution when the CO_2 pressure is exactly 0.000369 atm. This transition pressure increases rapidly with rise of temperature because K_w^2/nk_1k_2 increases rapidly while K_{Mg}/c varies little; the increase cannot, however, be calculated because the rate of increase of k_2 with temperature is not known.

From the values of the ion-concentrations computed by means of the above equations, the total amount of magnesium in solution was obtained by correcting for the ionization of $\text{Mg}(\text{HCO}_3)_2$ and MgCO_3 at their respective concentrations. This was done by dividing the value of (a) $\frac{1}{2}[\text{HCO}_3^-]$ (b) $[\text{CO}_3^{--}]$ by the appropriate fractional ionization (γ_1 and γ_2 , respectively), which was read from a curve obtained by plotting the fractional ionization—as derived from the conductivity of solutions of (a)

¹ The numerical values refer to $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at 18° ; c has been taken as 0.041. Cf. p. 2011.

² This value is the lower of the two given in Landolt-Börnstein-Roth Tabellen; it is due to Dupré and Bialas (*Z. angew. Chem.*, 16, 55 (1903)).

MgCl₂ (b) MgSO₄—against the concentrations of Mg⁺⁺. The results of these calculations are presented in Table VIII.

TABLE VIII.—THE CALCULATED SOLUBILITY OF MgCO₃·3H₂O IN WATER AT 18° IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE *P* OF CO₂.

<i>P</i> .	[Mg ⁺⁺].	[HCO ₃ ⁻]/2.	[CO ₃ ⁼].	[OH ⁻] × 10 ⁻⁴ .	<i>γ</i> ₁ .	[Mg] as Mg(HCO ₃) ₂ .	<i>γ</i> ₂ .	[Mg] as MgCO ₃ .	Total [Mg].
0.00020	0.01275	0.00765	0.000509	3.07	0.827	0.00925	0.505	0.01008	0.01934
0.00025	0.01454	0.00895	0.000558	2.87	0.820	0.01091	0.495	0.01126	0.02218
0.00030	0.01620	0.01017	0.000602	2.72	0.815	0.01247	0.486	0.01238	0.02486
0.00035	0.01775	0.01134	0.000640	2.60	0.810	0.01400	0.477	0.01341	0.02742
0.00040	0.01862	0.01217	0.000644	2.44	0.807	0.01506	0.473	0.01361	0.02868
0.00045	0.01906	0.01275	0.000630	2.28	0.805	0.01583	0.470	0.01340	0.02924
0.00050	0.01947	0.01330	0.000616	2.13	0.804	0.01655	0.467	0.01320	0.02976

The last column gives the total concentration of magnesium in solution at 18° at the several partial pressures, the solid phase in equilibrium with the solution being MgCO₃·3H₂O at pressures above 0.00037, but Mg(OH)₂ when the pressure of CO₂ is less than 0.00037. Accordingly, if we keep the CO₂ pressure constant at *P* and evaporate off the water at 18° so slowly that equilibrium conditions are continuously attained, we shall obtain the following amounts of either Mg(OH)₂ or MgCO₃·3H₂O from one liter of the solution:

TABLE IX.

<i>P</i> .	Total [Mg].	Mg(OH) ₂ . g.	MgCO ₃ ·3H ₂ O. g.
0.00000	0.00015	0.0087
0.00020	0.01934	1.13
0.00025	0.02218	1.29
0.00030	0.02486	1.45
0.00035	0.02742	1.60
0.00040	0.02868	3.97
0.00045	0.02924	4.05
0.00050	0.02976	4.12

If the constant pressure were exactly the transition pressure, both solid phases would be formed; but if it is slightly above or below this limit, either carbonate or hydroxide would separate when the water is evaporated off. At higher temperatures this transition pressure is, as noted above, higher.

From the foregoing it is obvious that the ordinary methods of preparing magnesium carbonate (in which, it is safe to say, a state of equilibrium is not attained continuously) will yield a product contaminated with hydroxide, the amount of which will depend upon the mode of working generally, and upon the prevailing partial pressure of CO₂ over the liquid in particular; moreover, that this contamination can be avoided completely by working with a partial pressure *P* greater than a certain limit. This limit is readily calculable in each particular case from the equations on p. 2015; and without doubt one could easily devise a process of preparing

pure MgCO_3 in which one atmosphere of CO_2 would suffice to prevent the precipitation of hydroxide.

The quantitative results presented above may require modification by reason of the possible inaccuracy of some of the data involved; of these the one most open to question is the solubility of magnesium hydroxide in pure water, which would tend to be found too high owing to the circumstance that the amount of magnesium present in solution in contact with magnesium hydroxide is increased more than a hundredfold when the atmosphere in contact with the solution contains as little as 2 parts CO_2 per 10,000 (see Table IX). Again the results given are subject to the limitation that the only solid phases are $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$; when conditions are such that one solid phase is $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ or MgCO_3 , the appropriate solubility-products (which at present are not known, and differ from one another, except at the mutual transition points) must be employed. Moreover, if within any temperature or pressure range a definite crystalline basic carbonate should be capable of stable existence in contact with water,¹ it would have to be taken into account in calculations relative to those conditions. In any case the general conclusions derived from these theoretical considerations are in complete accord with the established behavior of magnesium carbonate,² and in particular give a rational way of accounting for the well-known indefinite character of the ordinary basic carbonates of magnesia.

The Deposit from Solutions Containing both Calcium and Magnesium Carbonates.

In any solution saturated with respect to both calcite and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ the ratio of the concentrations of Mg^{++} and Ca^{++} must have a definite value; for instance, at 16° , this ratio is

$$\frac{[\text{Mg}^{++}]}{[\text{Ca}^{++}]} = \frac{[\text{Mg}^{++}][\text{CO}_3^{--}]}{[\text{Ca}^{++}][\text{CO}_3^{--}]} = \frac{K_{\text{Mg}}}{K_{\text{Ca}}} = \frac{1.4 \times 10^{-4}}{1 \times 10^{-8}} = 14000.$$

So long as $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is the second solid phase this value is independent of the partial pressure of CO_2 , and varies relatively little with the temperature. From the foregoing it follows that if a solution containing only calcium and magnesium carbonates is evaporated down (or if the partial pressure of CO_2 is gradually reduced, or if both things happen simultaneously) at 16° , pure calcium carbonate³ will precipitate so long

¹ This is equivalent to the condition that such a basic carbonate should have a definite solubility in water or water containing CO_2 , it being the only solid phase present; this implies that its molar solubility must be less than $1/2 \sqrt{K_h}$, where K_h is the solubility-product constant of $\text{Mg}(\text{OH})_2$ at the temperature in question, for otherwise $\text{Mg}(\text{OH})_2$ would be precipitated and two solid phases would be present.

² See, for instance, Abegg's Handbuch, II, 2, 66-9 (1907).

³ Under certain circumstances this might come down as aragonite instead of calcite; but this makes no difference in principle to anything here stated, for the solubility of aragonite is apparently only about 10% greater than that of calcite. This whole question is being taken up in another paper now in preparation.

as the above ratio is less than 14000, as it would normally be in natural waters, provided always that the CO_2 pressure is sufficient to prevent precipitation of magnesium hydroxide; on the other hand, the order of precipitation will be reversed if the relative concentration of magnesium ion be greater than 14000 (e. g., by addition of a soluble magnesium salt). It is to be emphasized however that the foregoing deductions, which are valid only if the only solid phases separating are pure calcite and pure $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, would have to be modified if, for instance, MgCO_3 can occur to a slight extent in solid solution with calcite, a possibility suggested by certain geological observations.

But we have another state of affairs if the partial pressure of CO_2 is such that magnesium hydroxide may precipitate; and in actual practice this case may very readily occur, since the hydroxide appears when the partial pressure of CO_2 is about 0.00037, a proportion which is somewhat greater than that normally present in outside air. This again can be readily calculated. By combination of Equations I and X we obtain the relation

$$[\text{Ca}^{++}][\text{OH}^-]^2 = [\text{Ca}^{++}][\text{CO}_3^{--}] \times \frac{[\text{OH}^-]^2}{[\text{CO}_3^{--}]} = \frac{K_w^2 \cdot K_{\text{Ca}}}{n k_1 k_2 c P} = \frac{3.43 \times 10^{-19}}{P}$$

at 16° ; consequently for values of P less than 0.00037,

$$\frac{[\text{Mg}^{++}]}{[\text{Ca}^{++}]} = \frac{[\text{Mg}^{++}][\text{OH}^-]^2}{[\text{Ca}^{++}][\text{OH}^-]^2} = \frac{1.2 \times 10^{-11} P}{3.43 \times 10^{-19}} = 3.5 \times 10^7 P,$$

a ratio which decreases steadily as P is reduced. It follows from this that calcium carbonate precipitated from a solution containing magnesium may very readily be contaminated with appreciable proportions of magnesium hydroxide, which would be removed only slowly by repeated reprecipitations. That this actually occurs in the commercial manufacture of calcium carbonate is evident from the experience of Hostetter,¹ who found it a matter of considerable difficulty to buy calcium carbonate satisfactorily free from magnesia. But this trouble may be obviated very easily, namely by conducting the operations in such a way that the liquid is always saturated with CO_2 at a pressure above a certain limiting value; this limit, which increases with the temperature, cannot at present be specified very accurately, but is in all probability not greater than 1 atm. for any conditions likely to be encountered in actual practice.

Further discussion of the deposits resulting from the concentration of solutions containing both calcium and magnesium carbonates will be deferred for the present, as it necessitates the consideration of the solubility, and proneness to supersaturation, of the several forms of calcium and magnesium carbonates, as well as of the double carbonate dolomite;

¹ J. C. Hostetter, *J. Ind. Eng. Chem.*, 6, 392 (1914).

and the evidence on some of these points is unsatisfactory or lacking altogether.

The Solubility-Product Constant of other Carbonates.

For the sake of completeness, the solubility-product constant of barium carbonate has also been recalculated. The data, which again are due to Schloesing, and the derived quantities are presented in Table X, which is altogether similar to Table II, except that the ionization is, in this case, that of barium acetate at the equivalent concentration. The mean value from the six last experiments is $\pi r K_{Ba} = 3.95 \times 10^{-8}$, whence

$$[Ba^{++}][CO_3^{--}] = 7.0 \times 10^{-9} \text{ at } 16^\circ.$$

TABLE X.—CALCULATIONS ON THE BASIS OF SCHLOESING'S DATA ON THE SOLUBILITY OF $BaCO_3$ IN WATER CONTAINING cP MOLS CO_2 AT 16° ; $c = 0.0441$.

P. (Atm.)	Total [Ba]. Mols l.	Total [Ba(HCO ₃) ₂]. Mols l.	γ .	[HCO ₃ ⁻]/2.	[Ba ⁺⁺].	$\pi r K_{Ba}$.
0.000504	0.000601	0.000589	0.930	0.000548	0.000560	3.02×10^{-8}
0.000808	0.000732	0.000722	0.924	0.000667	0.000677	3.38
0.00333	0.00117	0.00116	0.915	0.001065	0.00107	3.31
0.01387	0.00196	0.00196	0.895	0.00175	0.00175	3.51
0.0282	0.00255	0.00255	0.884	0.00225	0.00225	3.66
0.0499	0.00312	0.00312	0.875	0.00273	0.00273	3.70
0.1417	0.00464	0.00464	0.850	0.00394	0.00394	3.92
0.2529	0.00578	0.00578	0.838	0.00485	0.00485	4.09
0.4217	0.00690	0.00690	0.825	0.00570	0.00570	3.98
0.5529	0.00766	0.00766	0.818	0.00627	0.00627	4.05
0.7292	0.00843	0.00843	0.811	0.00684	0.00684	3.98
0.982	0.00941	0.00941	0.802	0.00755	0.00755	3.98

$$3.95 \times 10^{-8}$$

The constants of two other carbonates are known approximately;¹ namely, for silver carbonate,² for which it is about 10^{-12} , and for lead carbonate,³ about 10^{-14} .

Summary.

The solubility-product constants of calcium carbonate (calcite) and of magnesium carbonate ($MgCO_3 \cdot 3H_2O$), a knowledge of which is of importance in connection with several problems of geological interest, have been recomputed from the best experimental data available; the results are satisfactorily concordant. This concordance is the more remarkable in view of the fact that in the case of the data for calcium carbonate the

¹ Approximately only, because the partial pressure of CO_2 (which, however, would be small) was neither controlled nor measured.

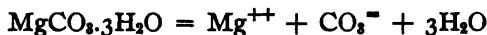
² Abegg and Cox, *Z. physik. Chem.*, 46, 11 (1903); Spencer and Le Pla, *Z. anorg. Chem.*, 65, 14 (1910). It would be well worth while to repeat these measurements under carefully controlled conditions, especially at a series of temperatures; for a number of important deductions could be drawn from the results.

³ Fleissner, *Arbeiten kais. Gesundheitsamt*, 26, 30 (1907).

partial pressure varies more than ten-thousandfold; while the total ion-concentration of all the magnesium carbonate solutions on which the actual solubility determinations were made, was more than 0.5 *N*. The recalculated results are: $[\text{Ca}^{++}][\text{CO}_3^{--}] = 0.98 \times 10^{-8}$ at 16°, when the solution is saturated with respect to calcite; $[\text{Mg}^{++}][\text{CO}_3^{--}] = 1.93 \times 10^{-4}$ at 12°, the solution being saturated with $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$; $[\text{Ba}^{++}][\text{CO}_3^{--}] = 7 \times 10^{-9}$ at 16°, the solid phase being BaCO_3 . The solubility-product constant K_{Mg} of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at temperatures up to 50° is given by the formula

$$\log K_{\text{Mg}} = 2315/T - 11.870,$$

whence the heat change corresponding to the reaction



is an evolution of 10600 cal.

With a knowledge of these constants and of the solubility-product constant of magnesium hydroxide, one can show that calcium carbonate precipitated from solutions containing magnesium is likely to be contaminated with small quantities of magnesium hydroxide which could be removed only slowly by reprecipitations as ordinarily carried out; that mixtures of magnesium carbonate and hydroxide will in general be obtained in the precipitation of magnesium by a carbonate and that the basic carbonates thus produced are merely indefinite mixtures of carbonate and hydroxide; and that both calcium and magnesium carbonates can be obtained free from contamination by keeping the partial pressure of carbon dioxide above a certain limiting value, the magnitude of which depends upon the conditions and in all probability need not be greater than 1 atm. by a suitable choice of mode of operation.

Incidentally the constant $[\text{HCO}_3^-]^2/[\text{CO}_3^{--}][\text{H}_2\text{CO}_3]$ was recalculated from McCoy's data, and found to be 5600 *n* at 25°, where *n* (which is in all likelihood greater than 0.5) is the proportion of the total CO_2 in solution which exists as H_2CO_3 ; whence k_2 , the second ionization constant of carbonic acid, is 6×10^{-11} , identical with the accepted value of this constant. It may be pointed out, moreover, that there can be no real *equilibrium* in aqueous solutions of carbonates except in presence of a definite partial pressure of CO_2 in the atmosphere in contact with the solution—in other words, that, strictly speaking, we are dealing with a ternary system, namely, base- CO_2 - H_2O ; consequently any carbonate solution through which a stream of gas absolutely free from CO_2 is passed, would gradually lose its carbonate and ultimately would contain only hydroxide.

ARSENIOUS OXIDE AS AN ALKALIMETRIC STANDARD.

BY ALAN W. C. MENZIES AND F. N. MCCARTHY.

Received June 25, 1915.

The fact that arsenic acid can be estimated volumetrically with an exceedingly sharp end point¹ suggested the possibility of the employment of this acid for purposes of standardization in alkalimetry. It is well known that arsenious oxide is a most desirable starting material in oxidimetry, and that the arsenious acid-iodine titration is one of the most accurate of the processes of volumetric analysis.² It will be shown below that arsenious oxide can be converted quantitatively into arsenic acid with comparative ease. This makes it possible to employ the same substance as a primary standard both in alkalimetry and in oxidimetry. A suitable procedure has been worked out for the standardization of an alkali solution starting from arsenious oxide, and the titer so found has been compared with that found for the same solution using three other methods of standardization of known accuracy.

Some Characteristics of Arsenious Oxide Desirable in a Primary Standard.—Arsenious oxide may be purchased commercially at a low price already in a high state of purity. It may readily be purified further both by recrystallization, if necessary, and by sublimation. The material used in our work was merely sublimed once, involving an astonishingly small amount of labor in view of the accuracy of the results obtained. White arsenic is not a hydrated substance, and can readily be dried by heating—the vapor pressure of the octahedral variety being at 200° and 240°, respectively, 0.6 and 6.0 mm. of mercury, while its melting point is 251°.³ The arsenic acid into which it is converted by oxidation is quickly and largely soluble⁴ in water, and yields a colorless solution.

Synthesis of a Decinormal Solution of Arsenic Acid.—The manipulation is simple and does not require, for example, the transference of a precipitate; but close attention to details is well repaid in saving of time.

In our work, a good commercial quality⁵ of arsenious oxide was purified by subliming once. To do this, a 6 × 1 in. test tube was drawn down to one-fourth of its bore at a point a couple of inches from the closed end, and the end pocket so formed was charged with white arsenic. The tube was clamped horizontally, suitably protected by asbestos paper above and set aside to heat over, but not in contact with, two lowered Bunsen flames. The sublimate was removed by cutting the tube at the constriction, dried by heating and bottled hot.

To prepare 500 cc. of 0.1 N solution, a quantity of about 2.47 g. of the

¹ Menzies and Potter, *THIS JOURNAL*, 34, 1452 (1912).

² Cf. Washburn, *Ibid.*, 30, 31 (1908).

³ Welch and Duschak, *Bur. Mines, Tech. Paper*, 81 (1915).

⁴ Menzies and Potter, *loc. cit.*

⁵ This was the "Arsenious Acid of Tested Purity" of Eimer and Amend.

powder is weighed out accurately in a 75 cc. conical flask. This is then treated with 5 cc. of chloride-free concentrated nitric acid, followed by 5 cc. of water¹ and warmed, at first gently, then more boldly, loss by spattering being prevented by a truncated calcium chloride tube.² When solution is complete, the further addition from a pipet of 5 cc. of concentrated nitric acid serves to wash the calcium chloride tube, which is now removed, and is necessary, also, to ensure complete oxidation. The solution is then taken to dryness to expel nitric acid. This part of the treatment is vastly expedited by blowing cotton-filtered, ammonia-free, air from a small glass jet obliquely on the surface of the liquid so as to cause rotation of the flask contents. The blower jet is clamped so that its twisted nozzle is close to the liquid surface, while the flask itself is clamped a couple of inches above a heated concave empty sandbath tray and screened from draughts by a glass cylinder consisting of a bottomless beaker. It was found that a thermometer whose bulb was placed alongside the bottom of the flask could register a temperature of 180–200° without any symptoms of ebullition appearing in the flask.

The dry white residue obtained in this manner still contains nitric acid that is not removable by heating at 230° for many hours. This nitric acid, possibly in solid solution,³ makes its presence evident not only by causing too high acidity but also by responding to the nitron test.⁴ The application of this test showed that the nitric acid can be removed, for analytical purposes, by redissolving the residue in water and taking to dryness again twice. For this purpose, after the first evaporation to dryness with nitric acid, the flask is allowed to cool, the residue is covered with distilled water and the flask then reheated as before. The residue soon dissolves, and the air-current evaporates the water again in a few minutes. This treatment with water is repeated, and it only remains to dissolve the residue and to dilute to the required weight or volume of solution.

The Process of Titration.—This has been described and discussed elsewhere,⁵ but may be again outlined for convenience. To a measured quantity of perhaps 30 or 40 cc. of the 0.1 *N* acid solution are added the phenolphthalein indicator and 3 or 4 cc. of saturated barium chloride solution—a quantity which is largely in excess of that required to form the permanent precipitate mentioned below. The alkali is then run in until the amorphous white precipitate formed locally becomes rather slow in redissolving, which occurs when about one-half of the required alkali has been added. At this stage the titration is interrupted and the vessel

¹ The nitric acid is added first as it wets the powder more effectively than does water.

² Cf. Gooch and Browning, *Am. J. Sci.*, [3] 29, 197.

³ Cf. Menzies and Potter, *loc. cit.*

⁴ Busch, *Ber.*, 38, 861 (1905).

⁵ See Menzies and Potter, *loc. cit.*

scratched beneath the surface of the clear liquid, if necessary, to induce the formation of the very characteristic lustrous silky crystalline precipitate of BaHAsO_4 , with respect to which the solution is supersaturated. After stirring for a minute to remove this supersaturation, the titration is completed in the usual manner. Should the vessel in which the titration is performed have been used for this type of titration already and merely rinsed with water, then the minute crystals of BaHAsO_4 remaining on the walls serve to inoculate their supersaturated solution and thus obviate any necessity for scratching. The entire proceeding is perfectly simple if only it be understood by the operator.

Comparison of Titre of Alkali as Standardized by this and by Other Methods.—The analytical details are tedious, as is their narration, which may, therefore, be curtailed. Weight burets were employed throughout, and quantities of 30–40 g. of solution were used in the analyses. As indicator 1 cc. of 0.1% phenolphthalein was employed, and a 7% transformation aimed at.¹ In making the corrections to vacuum, the densities of arsenious oxide and of benzoic acid were taken as 3.6 and 1.1, respectively. Carbonate-free sodium hydroxide containing barium hydroxide was employed as alkali, and the solutions were kept free from carbonic acid.

(I) The titre of the alkali was determined against suitably dried² benzoic acid³ by the method described by Morey.⁴ The 0.1 *N* factor for the alkali found in five determinations was, 1.0037, 1.0037, 1.0040, 1.0045, 1.0041; average, 1.0040.

(II) Hydrochloric acid of known concentration was prepared by the distillation method of Hulett and Bonner.⁵ The 0.1 *N* factor of this acid was thus, synthetically, 1.0028.

(III) The chloride in this acid was estimated gravimetrically, following as closely as possible the procedure of Morey⁶ in order to obtain results comparable with his. The 0.1 *N* factor of the acid obtained in four estimations was, 1.0028, 1.0030, 1.0034, 0.0020; average, 1.0026.

The titre of the alkali was now determined against this acid. Using 1.0026 as factor for the acid, six titrations gave, as 0.1 *N* factor for the alkali, —1.0042, 1.0035, 1.0038, 1.0039, 1.0036, 1.0035; average, 1.0037. Using an acid factor of 1.0028, this average would become 1.0039.

(IV) Five different solutions of arsenic acid were synthesized by the method described, and of each of these two titrations were made against

¹ Cf. A. A. Noyes, *THIS JOURNAL*, 32, 857 (1910).

² This drying requires care. Cf. Weaver, *Ibid.*, 35, 1309 (1913).

³ Purchased from the Bureau of Standards.

⁴ Morey, *THIS JOURNAL*, 34, 1027 (1912). To obtain a satisfactory color change of the indicator, it was found necessary to distill the laboratory alcohol over lime.

⁵ *THIS JOURNAL*, 31, 390 (1909).

⁶ *Loc. cit.*

the alkali, yielding the following figures for its 0.1 *N* factor: (1) 1.0039, 1.0045; (2) 1.0031, 1.0030; (3) 1.0037, 1.0033; (4) 1.0039, 1.0037; (5) 1.0035, 1.0033; average, 1.0036.

The results of standardizing the alkali by these various methods may be exhibited most clearly in tabular form:

Method.	0.1 <i>N</i> alkali factor.
I. Benzoic acid.....	1.0040
II. Hydrochloric acid, factor from constant boiling pressure.....	1.0039
III. Hydrochloric acid, factor from AgCl determination.....	1.0037
IV. Arsenic acid.....	1.0036

Summary.

It has been pointed out that arsenious oxide is a desirable substance for use as a primary standard in volumetric analysis; and it has been shown that it may be employed, without too complicated manipulation, for this purpose in alkalimetry.

PRINCETON, N. J.

COAGULATION OF ARSENIOS SULFIDE SOL BY ELECTROLYTES.

By JNANENDRANATH MUKHOPADHYAYA.

Received February 22, 1915.

The coagulation of arsenious sulphide sol by electrolytes has been studied by a number of investigators,¹ who observed certain peculiarities which led the present writer to undertake a study of the coagulation phenomenon in detail.

The sols examined were prepared in the way given by Linder and Picton; the water used was obtained by the method described by Jones and Mackay.² Two sols were prepared, one containing 32.9 (No. I) the other (No. IV) a very fine one containing 3.54 millimols As_2S_3 per liter. Nos. II and III were made by diluting No. I four times and twenty times respectively. Series of parallel experiments were made, in which equal depths of liquid contained in similar test tubes were observed and compared; very slight changes in the sol can be detected if comparison is made between the sample under observation and a blank with water added in place of the electrolyte solution.

Influence of the Quality of the Sol.—The changes observed on addition of an electrolyte are that after a certain time, depending on the concentration of the electrolyte, an increased turbidity is perceptible; this turbidity increases until the sol becomes almost, or even completely opaque. The maximum opacity depends upon the quality of the original

¹ Schulze, *J. prakt. Chem.*, 25, 431; Linder and Picton, *J. Chem. Soc.*, 61, 1117 (1892); 67, 63 (1895); Freundlich, *Z. physik. Chem.*, 44, 129 (1903); 73, 385 (1908); 83, 97 (1913); 86, 458 (1914).

² *Z. physik. Chem.*, 14, 317 (1894).

sol. There then appears a net-like formation throughout the sol which, if left undisturbed, becomes more and more coarse; this portion of the change can be followed with the microscope when the sol is dilute, but the later stages can be observed directly. A heterogeneous structure, attended by a diminution in opacity, is noticeable; the time when this maximum opacity is reached gives an idea of the progress of the process of coalition.

The next characteristic change observable is that this net-like structure begins to settle as a clot. This is accompanied by the appearance at the topmost layers of a visible net or membrane-like structure, separating a clear layer of liquid at the upper part from the turbid layers. The depth of this layer increases with time, and finally the whole settles to the bottom. The settling of the clot is irregular. It sometimes sticks to the side of the tube but on mere shaking, breaks up into flocks coarse enough to settle in a short time or even instantaneously. The time for its complete settling is not characteristic of the rate of coagulation; but that required for the appearance of perceptible change or for the attainment of the maximum opacity or for the beginning of the settling yields a definite idea of the rate of the change.

With concentrated sols the above changes are somewhat masked, especially the appearance of the maximum opacity. This is because such sols soon become opaque and further change cannot be followed; moreover there is then no perfect clearance but the upper layers remain slightly turbid. Such behavior is due to the fact that the process of coalition, even when far from complete, advances sufficiently to produce, with such sols, formations which have a visible rate of settling. The upper, clearer layers look quite clear in transmitted light; the *process of coagulation of this remaining portion of the sol begins anew, and thus the coagulation goes on in stages until finally we have the complete separation of the colloid.* With fairly dilute sols the above phenomenon is not so marked; hence in such cases formation of clots settling at a visible rate would require almost the completion of the process of coalition. However, with solutions of electrolytes such that the rate of coalition is very slow the above phenomenon occurs even with dilute sols. Here the maximum of opacity is to be looked for at the lower parts of the tube. The settling or sedimentation plays an extremely small part in the coagulation of colloidal arsenious sulfide.

The series of Sols I, II and III show that the concentration of electrolyte required to produce any change in a given time increases with the dilution of the sol. For equal concentrations of electrolyte the time for complete separation of the colloid may vary from a few minutes to about a month, according to the dilution of the sol. Thus with $N/16$ NaCl, As_2S_3 begins to separate from Sol I in 10 minutes, from Sol II after more than a day, and from Sol III not unless full 10 days have elapsed.

How rapidly the time for visible change, or the beginning of the separation of the colloid, changes with concentration of electrolyte, will be clear from the following example: With Sol III a concentration of $N/10$ NaCl produces visible change in a few seconds but with $N/16$ NaCl the change is not noticeable after six hours, and with $N/22$ NaCl noticeable change takes place only after four days. The variation of the concentration of added electrolyte has a much more marked effect on the stability of the sol than the variation of the concentration of the sol. The influence of the fineness of the sol in determining its stability is apparent when comparison is made between Sol IV and Sol I or Sol II. Sol IV contains less As_2S_3 than Sol II, but is not more stable to electrolytes than Sol II. Another peculiarity that strikes one on comparing Sol I and Sol IV, is that, whereas at lower dilutions of the electrolyte both sols show nearly equal stability, at higher dilutions Sol I increases in stability at a remarkably greater rate than Sol IV. Freundlich¹ found, contrary to what has been recorded above, that with decreasing concentration of the sol the concentration of electrolyte required to coagulate it decreases in a regular way; he refers this difference in the concentration of the electrolyte to increased adsorption in the more concentrated sol, due to the increased surface. Woudstra,² Reissig³ and others have, however, observed that the greater the concentration of the colloid the less the amount of the electrolytic required to coagulate it.

On the other hand it appears that the increase of stability with dilution of the sol is what should be expected. The facility for the coalition of the colloidal particles certainly decreases with increasing mutual distance between them resulting from dilution. With increasing fineness of a sol the concentration of the colloid remaining the same, the distance between individual particles decreases and hence the facility for the coalition increases. The increased Brownian movement also facilitates encounter between the particles. The progress and the visibility of the change in the colloid certainly depend on the above factors. It may be here added that the rapidity with which sols become stable with increasing dilutions of electrolyte points to the fact that at a certain dilution of the electrolyte the sol is no longer affected.

The Method of Addition of the Electrolyte to the Sol.—The process of coagulation being irreversible with this sol, the addition of small quantities of an electrolyte of much higher concentration cannot fail to produce immediate changes, which the final concentration of electrolyte attained after the mixture is of itself not able to effect. This is more objectionable if the quantity of electrolyte is added in a small volume, as with increas-

¹ *Z. physik. Chem.*, **44**, 129 (1903).

² *Ibid.*, **61**, 607 (1908).

³ *Ann. Physik*, [4] **27**, 186 (1908).

in concentration of electrolyte its coagulative power increases very rapidly. Equal volumes of sol and electrolyte were taken and addition was effected in small quantities followed by a thorough mixing, the whole process not taking more than a minute.

It was decided to avoid this method of mixing altogether by actually producing the sol in the electrolyte solution as a medium in place of water. The behavior of sols prepared in this way was compared with that of sols produced in water and subsequently mixed with electrolyte solutions so as to yield the same total concentration of both colloid and electrolyte; differences were observed, but the results are not really comparable because the amount of free H_2S in the two series was not the same.

In order to determine the effect of free H_2S , a quantity of sol containing 53 millimoles As_2S_3 was prepared in the usual way, except that one portion of it was not freed from dissolved H_2S by a stream of hydrogen. The effect of addition of a series of concentrations of KCl to these two samples was then examined, and it was found that the two series of sols showed great differences in stability. The sol containing H_2S almost to saturation is remarkably more stable than that freed from H_2S . Thus there can remain no doubt as to the fact that dissolved H_2S increases the stability of As_2S_3 sol. The portion freed from H_2S by a stream of hydrogen was next saturated with H_2S and the original sol containing excess of H_2S freed from it by a stream of hydrogen. These on examination gave the same result, the sol now containing free H_2S being more stable of the two. The difference in stability is as marked as before.

That free arsenious oxide, either in solution or suspension, does not influence the stability of the sol to any noticeable extent was next proved in the following way: A sol of the same As_2S_3 content as Sol III was diluted in one case with equal volume of a freshly prepared As_2O_3 solution, and in another with equal volume of water. The behavior of these two samples did not show any noticeable difference when examined with a series of concentrations of KCl.

This peculiar influence of H_2S is very noteworthy in view of the opinion held by some authors that the presence of electrolyte in many colloids is a necessity. Acids like HCl have a great coagulative power, whereas H_2S has a stabilizing power. To this stabilizing influence of H_2S observed here, is to be attributed the success of previous investigators in preparing metallic sulfide sols of great concentration. Wessinger and Spring¹ prepared sols of metallic sulfides by washing sulfide precipitates with H_2S water. Later Linder and Picton² used this method in preparing sols of metal sulfides of great concentration.

¹ *Bull. soc. chim.*, 49, 452; 48, 166.

² *Trans. Chem. Soc.*, 1892, 138.

Relative Coagulative Powers of Different Electrolytes.—A comparison of the coagulative power of different electrolytes was next made. With concentrated sols very low concentrations of polyvalent metallic ions have to be used; to avoid this, the dilute Sol III was used. *It has been observed that the order of the relative coagulative powers of different electrolytes is independent of the quality of the sol.* To define the coagulative power of any given electrolyte, we have first to investigate the factors that determine it. It has been shown that it depends on the concentration, the fineness, and the H_2S content of the sol. Thus the coagulative power of any given electrolyte has not a definite value and varies with the above factors. We can speak of coagulative power with respect to a specific sol. For the same electrolyte the coagulative power is determined by the dilution of the electrolyte which would produce a certain change in the colloid. The general method is to find out the concentration of electrolyte that would instantaneously lead to complete separation of the colloid. But there are also other methods in vogue. The value for the coagulation dilution would thus vary according to the nature and magnitude of the change in the sol in terms of which the coagulative power of any electrolyte is measured, and also on the method used. As a result, comparison between the coagulative power of any electrolyte by different methods is not possible. The present work has observed that the order of the relative coagulative powers of different electrolytes is independent of the quality of the sol used. But the different methods do not even give the same order of the coagulative power as will be made clear from a comparison of the data obtainable on As₂S₃ sol.

TABLE I.—ORDER OF THE COAGULATIVE POWER OF VARIOUS ELECTROLYTES AS DETERMINED BY DIFFERENT METHODS.

	Linder and Picton. ¹	Freundlich. ¹	As observed in the course of this investigation.
Trivalent	$\left\{ \begin{array}{l} Al_2(SO_4)_3 \\ AlCl_3 \end{array} \right.$	$AlCl_3$	$Al_2(SO_4)_3$
Divalent	$\left\{ \begin{array}{l} BaCl_2 \\ SrCl_2 \\ MgSO_4 \end{array} \right.$	$\left\{ \begin{array}{l} SrCl_2 \\ BaCl_2 \\ MgSO_4 \end{array} \right.$	$\left\{ \begin{array}{l} Ba(ClO_3)_2 \\ BaCl_2 \\ SrCl_2 \\ MgSO_4 \end{array} \right.$
Monovalent	$\left\{ \begin{array}{l} HCl \\ NH_4Cl \\ KCl \\ KBr \\ KI \\ NaCl \\ KNO_3 \\ NaNO_3 \end{array} \right.$	$\left\{ \begin{array}{l} HCl \\ NH_4Cl \\ KI \\ KCl \\ KNO_3 \\ NaCl \\ LiCl \end{array} \right.$	$\left\{ \begin{array}{l} HCl \\ NH_4Cl \\ KCl \\ KNO_3 \\ KBr \\ NaCl \\ KI \\ NaNO_3 \\ LiCl \end{array} \right.$

¹ *Loc. cit.*

The difference comes out quite markedly if comparison is made of the actual figures for relative coagulative powers of the electrolytes. Very little doubt can exist as to the accuracy of the data given in the third column. Whetham's Law¹ is not in agreement with the measurements made by Freundlich or by the present author, though Linder's and Picton's data seems to support it fairly.

In the opinion of the author this discrepancy is due to certain defects inherent in the methods used. The method of titration of the sol with electrolyte used by Linder and Picton² and others has been repeated, and it has been observed that if use be made of different concentrations of the same electrolyte for titration of the same preparation of sol, the quantities of electrolyte required are not in inverse ratio of the concentration of the electrolyte—in other words, different final concentrations are required to produce the same effect. With such methods the comparison of coagulative powers is liable to be inaccurate. Moreover the end point of coagulation is not easy to follow and varies with the rate of shaking and the time allowed for titration. Evidence in support of these statements is afforded by Table II, in which a series of results obtained with Sol III are brought together.

Electric conductivity of mixtures of sols and electrolytes was measured. It was hoped that if adsorption of the electrolyte occurred to any extent it would be evident from the diminution of the conductivity. The results, however, prove that if adsorption takes place at all, it is very slight. As controls throughout this part of the work two series of solutions were examined. In one series a definite volume of As_2S_3 sol was mixed with a definite volume of an electrolyte of a certain concentration. In the other the same volume of conductivity water as that of As_2S_3 sol taken was mixed with the same volume of the electrolyte of the same concentration taken in the other series. The two samples were kept side by side in an asbestos box and the temperature during the measurement of conductivity was noted. Whenever difference in temperature between the two samples of more than 0.1° was observed, the data were rejected. In some cases the results were controlled for either samples by a second or even a third repetition. The values for the conductivity were found to be always constant in all such cases. The observed conductivity of the sol and electrolyte is always greater than that of the electrolyte itself. If, however, the conductivity of an equal volume of the sol diluted with the same volume of water as that of the electrolyte used, be added to the conductivity of the electrolyte we get the same value for the conductivity as that observed. This shows that the conductivity of the electrolyte changes little if at all. From an examination of various dilutions of the following

¹ *Phil. Mag.*, 48, 474 (1899).

² *Loc. cit.*

TABLE II.—OBSERVATIONS ON THE EFFECT OF ADDITION OF VARIOUS SALT SOLUTIONS ON THE BEHAVIOR OF SOL III.

Dilution of added salt.	Time required for perceptible change.	Approx. time for maximum opacity.	Dilution of added salt.	Time required for perceptible change.	Approx. time for maximum opacity.
$\text{Al}_2(\text{SO}_4)_3$					
20000	9 min.	17 hrs.	20	A few secs.	> 15 min.
10000	< 1 min.	31 min.	18	Inst.	9 min.
9000	A few secs.	20 min.	16	Inst.	3 min.
8000	Instantaneous	10 min.	15	Inst.	1 min.
7000	Instantaneous	4 min.	14	Inst.	Inst.
2000	Instantaneous	Inst.	KNO_3		
	$\text{Ba}(\text{ClO}_3)_2$		14	25 min.	34 hrs.
700	10 min.	13	8 min.	22 hrs.
600	A few secs.	4 min.	12	3 min.	13 hrs.
500	Inst.	2 min.	10	A few secs.	24 min.
400	Inst.	Inst.	9	Inst.	2 min.
	BaCl_2		8	Inst.	Inst.
700	15 min.	KBr		
600	A few secs.	8 min.	14	20 min.	30 hrs.
500	Inst.	4 min.	13	8 min.	18 hrs.
400	Inst.	1 min.	12	4 min.	10 hrs.
360	Inst.	Inst.	11	A few secs.	5 hrs.
			10	Inst.	32 min.
	SrCl_2		KI		
700	7 min.	55 min.	13	20 min.	26 hrs.
600	3 min.	24 min.	12	9 min.	...
500	A few secs.	13 min.	11	5 min.	10 hrs.
400	Inst.	6 min.	10	2 min.	5.5 hrs.
300	Inst.	2 min.	9	Inst.	7 min.
	MgSO_4		NaNO_3		
600	5 min.	38 min.	12	21 min.	25 hrs.
500	1 min.	20 min.	10	8 min.	10 hrs.
400	A few secs.	11 min.	9	3 min.	1.2 hrs.
200	Inst.	Inst.	8	A few secs.	8 min.
			7	Inst.	3 min.
			6	Inst.	1 min.
			LiCl		
			10	7 min.	15 hrs.
			9	5 min.	12 hrs.
			8	3 min.	6 hrs.
			7	A few secs.	< 3 hrs.
			6	Inst.	1 min.

electrolytes— KCl , HCl , BaCl_2 , SrCl_2 and $\text{Al}_2(\text{SO}_4)_3$ it was observed that the conductivity agrees with the sum of conductivities whether complete or partial separation of the colloid has taken place or not. This is also true for great dilutions of the electrolyte. Deviations from the additive rule were within the limits of experimental error. This shows that the conductivity of the sol is to be attributed not to the particles of the colloid, but to dissolved H_2S or As_2O_3 or anything else. The conductivity

the colloidal granules thus seems to be very small. Different sols were examined, but the nature of the results obtained was the same. From Dumansky's data¹ on conductivity measurements of colloidal $\text{Fe}(\text{OH})_3$, in presence of electrolytes, Wo. Ostwald² calculated the amount of adsorption by the colloid of those electrolytes which have a coagulating action on it. But, as we have seen, absolutely no change in conductivity is observed with As_2S_3 sols.

From data given by Linder and Picton it would appear that adsorption of barium takes place to a marked degree with liberation of an equivalent quantity of HCl . This adsorption with consequent liberation of Cl has been confirmed by Whitney³ and Duclaux.⁴ The author has not been able to confirm this, but it has been found that on washing carefully the precipitated As_2S_3 , the amount of barium in it is very small and scarcely capable of quantitative measurement. However, from a large quantity of precipitated As_2S_3 , an amount of barium was obtained which gave a slight turbidity with H_2SO_4 , but was too small for quantitative estimation. This quantity might as well have been adsorbed by the coagulated sol or due to chemical interaction with As_2S_3 , as Duclaux supposes.

Summary and Conclusion.

- (1) With dilution of sols of As_2S_3 the stability increases.
- (2) Fine sols are less stable than coarse sols of the same arsenious sulfide content.
- (3) Coagulation of colloidal arsenious sulfide with electrolytes is mainly a process of coalition of the colloidal particles. Coalition takes place through the substance of the sol with formations of definite clot-like structures. Sedimentation plays an extremely minor part in coagulation. The rate of coalition is determined by the concentration and nature of the electrolyte. With concentrated sols and relatively dilute electrolytes the coagulation goes on in stages till the complete separation of the colloid takes place.
- (4) Dissolved hydrogen sulfide has the interesting effect of markedly stabilizing arsenious sulfide sols against electrolytes.
- (5) Adsorption of electrolytes by the colloid does not take place to any marked extent as is proved from conductivity measurements and analysis.
- (6) The order of the relative coagulative powers of various electrolytes is different as determined by different methods.

My best thanks are due to Profs. Rây and Bhaduri.

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¹ *Z. Chem. Ind. Koll.*, 1, 281 (1906).

² *Gedenksboek Bemmelen*, 1910, 267.

³ *THIS JOURNAL*, 23, 842 (1901).

⁴ *J. chim. phys.*, 6, 592 (1908).

THE THERMOELECTRIC PROPERTIES OF CARBON.¹

By WILLIAM C. MOORE.

Received June 8, 1915.

In an attempt to learn something of the nature of the so-called amorphous carbon, an investigation of the thermoelectric properties of commercial arc carbons was begun in this laboratory in the early part of 1914. It is true that some work of this type had been previously reported upon by others, but the work of Buchanan,² is open to the objection that the carbon rods were used in series in measuring the thermal electromotive force of a carbon platinum couple, thus introducing the possibility of getting potential differences between the carbon rods themselves; while Monckman³ measured the potential set up when a hot carbon rod was touched against a cold rod of similar material, without actually measuring the electromotive force set up when his carbon rod was an element of a couple employed in the usual way.

Monckman observed a change in sign of his galvanometer deflection when the hot rod was at 480° and the cold at 16°, and, assuming a gradual regular rise and fall of the thermal electromotive force, decided that the neutral point must have been in the neighborhood of 250° and that this indicated a change in the properties of carbon at that point.

While our investigation was under way, an article by Bidwell on "Thermojunction of Carbon and Graphite"⁴ appeared. This investigation noted that heating his carbon and graphite rods to near 2000° made the thermoelectric behavior more regular and attributed this to the expulsion of impurities. Differences in the original raw materials used in the manufacture of the carbons and changes in the nature of the carbon, except graphitization, were not taken into account by Bidwell. There is abundant evidence, however, that heating does actually change the properties of carbon,⁵ and there is likewise some previous evidence that some of these changes are reversible.⁶

This evidence seems to be substantiated by our experiments, which covered a period of several months. During this time a large number of measurements were made on various kinds of arc carbons. A summary

¹ Read in abstract at the New Orleans meeting of the American Chemical Society.

² *Phil. Mag.*, [5] 20, 117 (1883).

³ *Proc. Roy. Soc. London (A)*, 44, 220 (1888).

⁴ *Phys. Rev.*, [2] 3, 450 (1914).

⁵ See Moissan, "The Electric Furnace" (Lenher's translation, p. 38, *et. seq.* (1907 ed.), as to the effect of heat on the properties of lamp black, and Buchanan, *Loc. cit.* as to changes in carbon filaments.

⁶ Manville's work on the variability of the temperature of combustion of charcoal when subjected to temperature fluctuations (*J. chim. phys.*, 5, 297-339 (1907)), and that of Brion (*Ann. der Phys.*, 59, 215 (1896)) on the effect of sudden changes of temperature on the resistance of carbon filaments, may be cited in this connection.

of some of our typical experiments may therefore be of interest from the light they shed on the nature of amorphous carbon.

Experimental.

In the preliminary experiments, six arc carbons were used, two of which were of the same kind of carbon. These six pieces may be designated as 1, A, B, C, D, and E, respectively. A, B, C, D, and E were clamped in turn against 1; leads were fastened to the free ends, and the circuit completed through a millivoltmeter used as a galvanometer. The clamped ends were heated by a Meker burner. In every couple, except that formed by 1 and B, which were of the same kind of carbon material, there was developed considerable electromotive force. Carbon 1 was positive at the cold end in all cases except when E was the other member of the couple. In this case E was positive, and the electromotive force was greater than with any of the other couples.

C and E were now made into a couple; after 42 minutes' heating (to low redness) in the flame of a Meker burner, the thermal electromotive force had risen to about 7.25 millivolts, E of course being positive. A number of runs were then made, using various combinations of carbon to make the thermojunctions. The couple burned very rapidly at the higher temperatures. From carbon-carbon couples it was a natural step to carbon-copper couples. The burning of the carbon and the oxidation of the copper were so serious, however, that it was finally decided to make up couples by inserting the carbon into a long copper tube, $\frac{7}{8}$ inch internal diameter, and closed at the end to be heated. Contact between the carbon and copper was secured by flattening the closed end of the tube and forcing the wedge-shaped end of the carbon into this angle. The carbon was held in place by a brass rod which passed through a rubber stopper closing the copper tube. This rod was soldered at its inner end to a brass cap which made a tight contact over the end of the carbon, and served as a terminal for the carbon cold junction. The cold junction was kept cool by a stream of water playing over the copper tube. In making an experiment the air was continuously exhausted by means of a water pump. The copper tube showed a little leakage in some of the experiments but, even when leaking a little, protected the carbon from burning. It was noted that at the higher temperatures, the carbon became "copper plated" over a large portion of its length. The thermal electromotive force was measured by means of a high resistance Siemens-Malske¹ millivoltmeter; furnace temperatures by a bare base metal thermocouple. Above 600° these temperatures are accurate to within about

¹ In order to guard against changes of contact resistance, special care was taken to see that all contacts were well made, and in one case it was found that the resistance of a carbon-copper couple changed from 0.306 ohms at room temperature to 0.27 ohms at 720°.

15°; below that temperature, probably within 5 to 8 degrees. A Hoskins FB 204 electric furnace was used as the heating device. The copper tube and the thermocouple were in close proximity; each was immersed ten inches in the furnace.

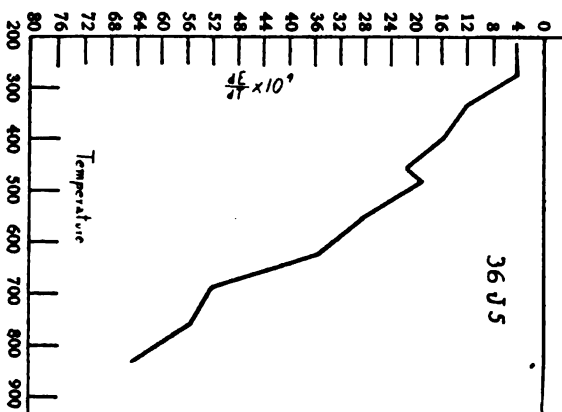
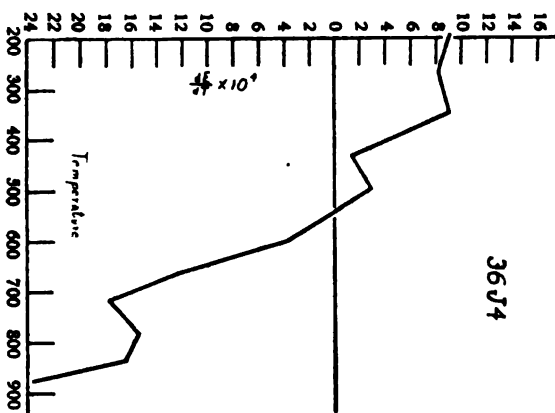
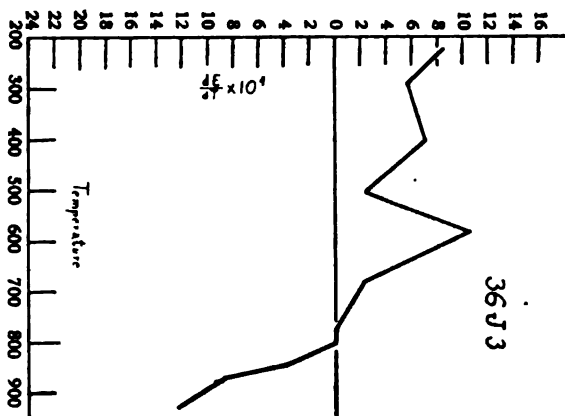
Table I gives a summary of the results obtained. The carbon used in Experiment 36J3 was of a different composition from the carbons used in 36J4 and 36J5. The thermal histories of these three carbons were different, but each carbon had been previously heated to a temperature higher than that finally reached in the experiments. We might also add that the maximum temperatures recorded below were purely fortuitous.

TABLE I.

Expt. No.	Initial furnace temp.	Initial E. M. F. (M. V.)	Temp. difference at point max. E. M. F.		Fur. temp. at max. E. M. F.		Max. E. M. F. millivolts.
			Beginning.	Ending.	Begin.	Ending.	
36J3	157°	+0.08	717°	784°	741°	816°	+0.41
36J4	157°	+0.09	478°	528.5°	514°	565°	+0.30
36J5	169°	-0.06	-2.18

Expt. No.	Polarity.		Max. fur. temp.	E. M. F. at max. temp. (millivolts).
	Initial.	Final.		
36J3	Cu.+	Cu.+	945°	+0.32
36J4	Cu.+	Cu.-	910°	-0.21
36J5	Cu.-	Cu.-	878°	-2.18

Explanation of Table and Discussion of Results.—The first three columns need no explanation. The fourth column shows the difference in temperature, of the hot and cold carbon-copper junctions, when the thermal electromotive force reached a maximum. This occurred only in Expts. 36J3 and 36J4. This maximum electromotive force remained constant over a considerable temperature range, and began to decrease when the temperature differences between the hot and cold carbon-copper junctions reached the values shown in the fifth column. The sixth and seventh columns show the actual furnace temperatures (\pm about 8°), at the beginning and end of this constant temperature interval, respectively. The other columns need no especial comments. This table shows most of the striking features exhibited by various carbon-copper thermocouples. It should be added, that the readings obtained with an individual carbon are approximately reproduceable. For instance, in Expt. 36-2-A in which a carbon-copper couple was used, several runs were made with the same couple, readings being taken both with rising and falling temperatures. Here, readings of 3.24 millivolts were obtained at the following temperature differences, the starred values being for falling temperatures in the furnace: 321°, *314°, 323°; and readings of 2.40 millivolts at temperature differences of 256° and *258°. In 36J3 after 945° was reached, the furnace was allowed to cool and the electro-



motive force rose. When the temperature difference was 839° the electromotive force was 0.40 as against the same value, for a temperature difference of 847° , on the rising temperature.

If a carbon-carbon couple be set up, using different kinds of carbon, we may get very high electromotive forces. One couple of this type gave 14.59 M. V. when the cold junction was at 55.5° and the hot junction was at 707° .

It will be noted in the above table that there was a considerable temperature interval over which the electromotive force remained constant in the two experiments, 36J3 and 36J4. This means, that the temperature coefficient of the thermal electromotive force remains at zero throughout a considerable temperature range. The attempt was made to plot the temperature coefficient of the potential, against temperature. The potential in most cases was so small, however, that steps of 50° or more were necessary to get any curve at all, and after plotting, the curves were very irregular, especially at the lower temperatures. For 36J3 the temperature interval for zero temperature coefficient was from 775° to 805° while for 36J4, the point of zero coefficient was at 540° . It may be said, however, that the general directions of the temperature-coefficient temperature curves change for these two experiments, after passing through the zero point. For 36J5 all the potential values were such that the temperature coefficient was entirely negative, and the rough curve for the experiment was more nearly a straight line than with 36J3 and 36J4. These rough curves are shown in the appended figures.

The thermoelectric properties of various kinds of arc carbons are thus seen to differ considerably. These differences are in general due to two causes, (a) difference in raw materials used, and (b) differences in manufacturing history.

The general change of direction of our temperature-coefficient temperature curves mentioned as being noted in Experiments 36J3 and 36J4 taken with the long temperature interval of constant electromotive force for these couples, suggests that possibly some constituent of our carbon may have passed through a transition interval in the temperature region noted. Whether this constituent is a form of carbon or a complex compound of carbon is of course unknown.

Summary.

This study of the thermoelectric properties of carbon offers evidence from a new viewpoint that amorphous carbon is not a single definite substance. The thermoelectric properties of this material are reproducible for any one carbon, but they may vary with the temperature and are determined by the kind of raw material used and the manufacturing history of the carbon. The fact that with some varieties of arc carbons a considerable temperature range of constant electromotive

force was found, indicates the possibility of a transition interval for these carbons.

The author's thanks are due his assistant, Mr. J. B. Davies, for much of the painstaking experimental work involved, and Mr. W. R. Mott for aid in looking up the literature.

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A NEW CRYSTALLINE VARIETY OF SILVER.

BY TARINI CHARAN CHOUHRI.

Received July 6, 1915.

Various modifications of silver, many of them of somewhat ill-defined character, have, from time to time, been described.¹ Carey Lea has carried out an extensive series of researches on the properties of silver precipitated from a solution of its salts by ferrous citrate, ferrous tartrate, etc., in the presence of alkalis. His colloidal silver, which is held to be an allotropic modification of the metal, displays almost every shade of color—blue, red, green, purple and golden; some of his "precipitates" are very soluble in water and very sensitive to light. According to Lüdtkke,² however, the mirror and the black silver, obtained by the reduction of silver nitrate with zinc, are allotropic modifications, while the work of Kohlschütter and Fischmann is an attempt to explain the way in which the specular form of native silver, known as hair-silver, is formed.

Experimental.

Spongy silver³ was first prepared by igniting pure and dry precipitated silver tartrate in a crucible. Nitric acid, diluted with an equal volume of water, dissolved the silver completely. Strong nitric acid (sp. gr. 1.42), however, from which lower oxides of nitrogen were removed by boiling with carbamide, was allowed to act on the spongy silver at the ordinary temperature. At first some action took place with the formation of silver nitrate, nitrous acid and oxides of nitrogen; but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about a fortnight, the remaining silver was converted into long needle-shaped crystals—easily visible to the naked eye.

At first a few thin, needle-shaped crystals appeared floating on the surface of the acid liquid which was being shaken; the test tube being allowed to stand again for some time, the crystals gradually increased in quantity, the larger needles remaining at the bottom of the tube. The nitric acid was decanted off and the crystals were thoroughly washed with

¹ Carey Lea, *Am. J. Sci.*, 37, 476; 38, 47, 129 (1889); *Phil. Mag.*, 31, 238, 320, 397; 32, 337 (1891); *Am. J. Sci.*, 48, 343 (1894); Lüdtkke, *Wied. Ann.*, 92, 152, 1056 (1894); Kohlschütter and Fischmann, *Ann.*, 387, 86 (1912).

² *Wied. Ann.*, 50, 678 (1883).

³ The spongy silver examined under the microscope showed no crystalline structure.

distilled water. They had the characteristic white metallic lustre of silver and belonged to the cubic system. The following experiments show that the crystals are nothing but metallic silver:

(1) A weighed quantity of the crystals was heated on a small cupel in a muffle furnace and the button of silver obtained was weighed:

0.1370 gave 0.1361 Ag : Ag = 99.34%.

(2) A weighed quantity was dissolved in moderately strong nitric acid and the silver precipitated and weighed as silver chloride:

0.2840 gave 0.2826 AgCl : Ag = 99.50%.

This is considered to be a new variety of crystalline silver. Ordinary metallic silver consists of rhombic plates¹ which, however, in form and in the mode of formation are quite different. Kohlschütter and Fischmann have described a variety termed hair-silver, but they have only been able to obtain this from silver sulfide or selenide at temperature of about 400°.

Bearing on the Dynamic Theory of Allotropy.

It has been observed, as referred to before, that the tiny needle-shaped crystals which were first formed, appeared on the surface of the column of liquid, so that the crystalline silver does not (at the moment of formation) co-exist with the spongy silver at the bottom of the vessel. It has also been observed that the spongy silver at the bottom gradually crumbles into a finer state of division, looking amorphous under the microscope and this gradually diminishes in quantity, giving rise to crystalline needles at the surface.

As the conversion of spongy silver into crystalline variety takes place at the ordinary temperature in a heterogeneous system, Smits' dynamic theory of allotropy is not applicable to the present case. According to Smits, the transformation of one form into an allotrope is not a sudden process and at the high transformation temperature (*e. g.*, of rhombic sulfur into monoclinic and *vice versa*) each variety is partially miscible in the other at the high transition-temperature, and equilibrium, according to him, being established between different proportions of the different varieties. Benedict also holds somewhat similar views. But such ideas are evidently not applicable to the present case. Tammann's view however, applies better. According to him, allotropic change is due to difference in atomistic arrangements, and it is probable in the present case that the solution-tension of metallic silver at the particular condition being small, the particles of silver, which are first produced from spongy silver, are drawn up by the capillary force of the liquid column to its surface where they orient themselves regularly in a different space-lattice, giving rise to the beautiful needles.

¹ Hiorns' "Metallography:" Silver.

Summary.

Spongy silver, prepared by igniting pure silver tartrate, was treated at the ordinary temperature with strong nitric acid (sp. gr. 1.42) from which lower oxides of nitrogen had been removed by boiling with carbamide. At first some action took place with the formation of silver nitrate and nitrous acid, but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about two weeks, the remaining silver was converted into long needle-shaped crystals easily visible to the naked eye; slender needles which are first formed, appear floating on the surface of the acid liquid. This is considered to be a new variety of crystalline silver, belonging to the cubical system.

The author desires to express his indebtedness to his professor, Dr. R. R. Watson, who took an active interest in course of this work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

CAN THE DISSOCIATION THEORY BE APPLIED TO SOLID SOLUTIONS IN STEELS?

BY EDWARD D. CAMPBELL.

Received June 19, 1915.

The conception that many metals and alloys might be regarded as solidified solutions, either of miscible liquids or of compounds in solution, was clearly pointed out more than fifty years ago by A. Matthiessen.¹ Under this conception pure or nearly pure metals and alloys would be regarded as liquids or mixtures of liquids, differing from ordinary ones only in viscosity, but still being solutions in which the atomic relations existing between solutes and solvent do not differ fundamentally from the same relations in ordinary solutions. Matthiessen made numerous measurements on the conductivity of metals and alloys but drew no general conclusions as to the relation between chemical constitution and electrical properties.

Some twenty years later, Barus and Strouhal² carried on a long series of very careful experiments to show the relation existing between the hardness of tool steel and its electrical properties. The changes in specific resistance in tool steel induced by sudden quenching and reheating to various temperatures for different lengths of time were carefully investigated, but apparently no definite connection between change in specific resistance and chemical constitution was pointed out.

¹ Report of the British Association for the Advancement of Science, 1863, p. 37.

² U. S. Geological Survey, *Bull.* 14, 1885.

Barus endeavored to show that the hardness of steel is a function of the specific resistance. If by the hardness of steel is, in reality, meant viscosity, that is, the resistance to flow under high pressure as applied in a Brinell ball testing machine, then the hardness is not a function of the specific resistance, since the latter in a piece of hardened steel may be reduced by moderate tempering more than 40% without any measurable reduction in the hardness.

The hardness of steel is becoming generally recognized to be due to a certain portion of the iron existing in a state of strain, the extent of which internal tension or interstrain is dependent upon the chemical constitution at the instant of quenching and the rate of cooling through the critical range. Iron lends itself perhaps better than any other metal to a study in solid solution, since iron exists in the two well-known allotropic forms, the stable alpha form, soft, magnetic and of low solvent power and the gamma form, probably somewhat harder than the alpha, nonmagnetic, and possessing at least ten times the solvent power of iron in the alpha condition. Pure iron when converted into the gamma form by heating above the A_{c3} critical point, is transformed on cooling through the critical range into the alpha form with such velocity that, no matter how quickly cooled, there is but little evidence of the presence of gamma iron in the cold specimen. The rate of transformation of the gamma into the alpha form, when passing through the critical range is very markedly influenced by the presence of solutes, particularly carbides in solid solution, and it is largely through control of the concentration of solutes at the instant of quenching that the extent of transformation of the gamma into the alpha form, hence the extent of internal or interstrain, and thus the hardness, is controlled.

If a piece of steel of moderate carbon content be very quickly cooled from a temperature sufficiently above the critical range to insure complete solid solution of the carbides, the quenched metal will consist of an unstable solid solution of carbides in gamma iron, together with some alpha iron in the state of strain. If, on the other hand, the same steel were cooled slowly through the critical range, the gamma iron would be completely transformed to the alpha form and the carbides, in consequence of their slight solubility in alpha iron, would be almost completely precipitated.

The object of the experimental work described in this paper, which was carried on by Mr. Robert Atkinson, was to bring out the relation which exists between the concentration of the carbides in solid solution in steel and the specific resistance.

In the well-known colorimetric method for the estimation of carbon in steel, the brown color of the dinitro derivatives produced by the interaction of nitric acid on the iron and the unsaturated hydrocarbons de-

rived from the carbides, is used as a basis for determining the percentage of carbon in the steel. It has been well known for many years that if even reasonably accurate results are to be obtained, the unknown steel and the standard steel, if a steel standard is used, must both have approximately the same composition and be subjected to approximately the same heat treatment. If the color of the dinitro derivatives obtained by dissolving a sample of steel in nitric acid is compared with that of a mixed solution of ferric, cupric and cobaltous chlorides, made up as a permanent color standard, the absolute value of each scale division of a colorimeter in terms of carbon percentage cannot be expressed as a constant, since the molecular weight of the carbides, hence that of the hydrocarbons from which the dinitro derivatives are formed, will vary with the carbon content and heat-treatment of the steel.

In an article, "The Effect of Heat Treatment on the Colorimetric Test for Carbon in a 0.32 Carbon Steel,"¹ details are given showing the method of analysis used in the present work to estimate colorimetrically, the quantity of dinitro compounds derived from carbides soluble in cold nitric acid and those insoluble in cold but soluble on heating for thirty minutes in boiling water. The depth of color was estimated by comparison with a standard solution of ferric, cupric and cobaltous chlorides, contained in a modified colorimeter,² the strength of the chloride solution being such that one scale division of the colorimeter was equivalent to a little less than 0.01% carbon when a sample of 0.250 g. of the steel was used.

The steel used in these experiments, which for convenience has been termed H 35, was furnished through the courtesy of the Halcomb Steel Company and has the following composition: Carbon, 0.35; manganese, 0.08; phosphorus, 0.009; sulfur, 0.024; silicon, 0.18. Bars of this steel about 15 cm. long and a little over 6 mm. square were suspended in an electrically heated furnace, so arranged that oxidation during heating was completely avoided. The temperature of the bars was measured by means of a standard platinum rhodium thermocouple placed close to them. They were allowed to remain in the furnace one hour to attain the same temperature as that indicated by the thermocouple, 892°, after which they were quickly removed and quenched in a large excess of water. The temperature of the water at the beginning was +4° and at the conclusion of the work about +14°. The time required to transfer a specimen from the furnace to the quenching bath, taken with a stop watch, averaged four-fifths of a second. From the time the specimen entered the water until it was black was from four-fifths of a second to one second, while between five and six seconds were required to bring it to the tempera-

¹ *J. Iron and Steel Inst.*, 2, 367-84 (1913).

² *THIS JOURNAL*, 33, 1112 (1911).

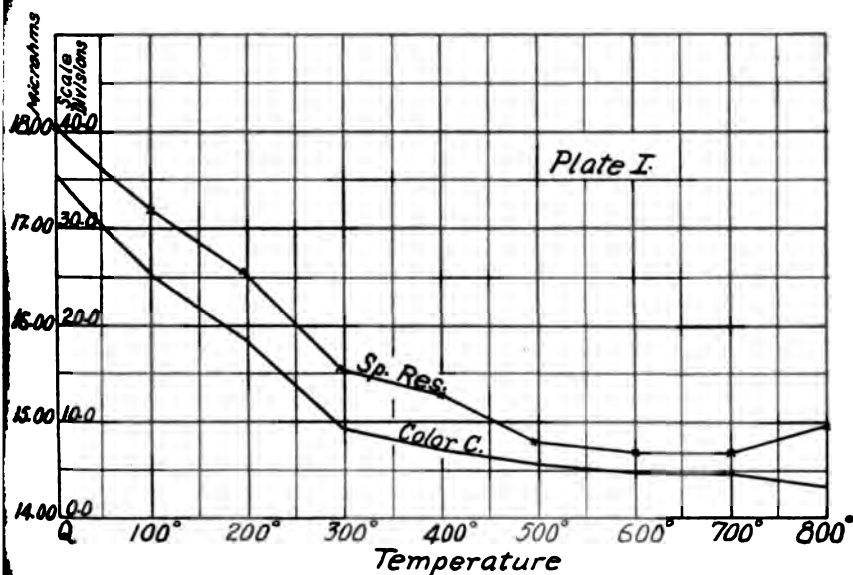
ture of the bath. No oxidation took place during the time the bars were in the furnace, and the film of oxide which formed on the surface during the time the bars were being transferred from the furnace to the quenching bath was so slight as to be only a discoloration. After quenching, the bars were polished and the specific resistance determined. Sufficient drillings were taken from one bar to make the necessary colorimetric determinations. The specific resistance was determined by measuring the fall in potential between knife edges 10 cm. apart on bars of accurately measured cross-section, while a known current was flowing through them. The knife edges were bolted to a small glass plate, thus insuring constancy of distance apart, and the bars during measurements were immersed in a bath of refined, paraffin oil, so that their temperature could be determined and all readings reduced to a standard of 20°. The fall in potential was compared with that of a standard resistance bar calibrated by means of a standard potentiometer and certified standard cell. Duplicate determinations could be easily kept within 0.05 microhms and it is thought that the absolute values of resistance are correct within less than 0.2 of a microhm. After measuring the specific resistance and taking sufficient drillings for making colorimetric determinations, the quenched bars were placed in a steam drying oven at from 100–105° for two days, after which they were removed, the specific resistance measured and drillings taken for colorimetric work. In the subsequent heat treatments the bars from the previous treatment were packed in a steel tube to avoid oxidation, together with a tube for the insertion of a thermocouple and the whole placed in an electric furnace, which was then gradually raised to the temperatures shown in the table of specific resistances. When the desired temperature, as indicated by the thermocouple, was reached, it was held as nearly as possible for from one to two hours, after which the furnace was allowed to cool over night. After each heat treatment the specific resistance was again measured and drillings taken for colorimetric comparisons.

As it is impossible to express in absolute percentages the amount of carbon represented in the dinitro derivatives, the color due to these is expressed in scale divisions of the colorimeter. The results of the measurements are given in the following table, in which Column I shows the temperature to which the bars were reheated after quenching from 892°; Column II, the specific resistance in microhms per cm². at 20°; Column III, the amount of dinitro compounds derived from carbides soluble in cold nitric acid, expressed in scale divisions of the colorimeter; and Column IV, the amount of dinitro compounds derived from carbides insoluble in cold nitric acid, but soluble at the temperature of boiling water.

TABLE I.—SHOWING INFLUENCE OF HEAT TREATMENT ON SPECIFIC RESISTANCE AND COLOR TESTS.

Column I.	Column II.	Column III.	Column IV.
20°	18.07	35.2	12.8
100°	17.15	25.0
195°	16.57	18.5
295°	15.55	9.3
400°	15.30	6.7
492°	14.79	5.8
600°	14.67	4.6
700°	14.69	4.5
800°	14.95	3.0	39.0

The results given in Columns I, II and III of Table I are shown graphically in the accompanying Plate I, in which the abscissae represent the temperatures of reheating, while the ordinates show the specific resistance in microhms and the color of the dinitro derivatives due to carbides soluble in cold nitric acid, in scale divisions.



A study of the figures in Table I or, more easily, a glance at the curves in Plate I, reveals clearly the close relationship existing between the concentration of the carbides in solid solution and the specific resistance.

However, it will be noted that in the sample reheated to 800° there is an increase in specific resistance accompanied by a decrease in the dinitro derivatives. Metal cooled very slowly from 800° would have the carbides distinctly segregated into relatively large masses, and although the precipitation would be most nearly complete the separated cementite would

consist of carbides saturated with iron in solid solution; hence the increase in specific resistance.

The question may properly be asked, to what may this relationship probably be due? If a metal such as iron be regarded as a solvent, differing, it is true, in viscosity from ordinary liquids, but in which the atomic relations existing between solutes in true solid solution and the solvent are essentially the same as the relations existing in ordinary solution, we may find the reasonable explanation for the correlation between the concentration of the carbides in solid solution and the specific resistance of steel.

While in most research work in physical chemistry attention is focused on the solutes, and the influence of concentration, temperature, etc., on these, in most work in metallurgy attention is, perhaps unconsciously, focused on the properties of the solvent; and the influence of temperature and concentration of solutes on the properties of this latter is what is most carefully studied. It is seldom that ordinary chemistry is regarded as a study of the influence of solutes on the properties of water, and yet this is the habitual view-point taken in the study of the influence of impurities on the properties of metals. If iron is regarded from the same view-point as ordinary solutions, we may calculate the molar concentration of solutes in solid solution in a manner exactly similar to that employed in such calculations in ordinary solutions. If the assumption is made that one liter of steel weighs 7800 g., the molecular concentration of solutes in solid solution in iron would be represented by the following formulae given in the table below, in which the symbol of the element stands for the number of "points" (0.01%) of that element, and N , the number of atoms of the element in each molecule of the solute.

TABLE II.—SHOWING FORMULAE AND MOLECULAR CONCENTRATIONS OF STEEL, H 35

Element.	Formula.	Molecular concentration.
C.....	$\frac{C}{15.4 N}$	$\frac{2.27}{N}$
P.....	$\frac{P}{39.8 N}$	$\frac{0.02}{N}$
S.....	$\frac{S}{41.1 N}$	$\frac{0.06}{N}$
Si.....	$\frac{Si}{36.3 N}$	$\frac{0.49}{N}$

Manganese is not included in the above table since in steel it functions as a metal, entering partly into combination with carbon and sulfur and partly into the constitution of the solvent, iron, the law of mass action determining its distribution. The same law applies to the distribution of Ni, Cr, and some other elements frequently found in steel.

In an article on "The Constitution of Steel,"¹ it was shown that N of the above table in the case of carbides, is a function of the carbon content and heat treatment of the steel. In the case of a slowly cooled, low carbon steel, N is more than four (4), while in high carbon steel it averages less than this figure. In a metal suddenly cooled from above the critical point, the value of N is distinctly lower than when the same metal is in the annealed condition.

In the dissociation theory as applied to aqueous solutions, when solutes dissolve, a certain proportion of the molecules are assumed to be separated into parts, termed ions. When a solute is dissolved in water it dissociates to a large extent and the chemical or internal energy is decreased, with the appearance of equivalent quantities of electrical energy in the form of equivalent positive and negative charges on the respective ions. It is because the solvent in the case of an aqueous solution is a dielectric that the ions are able to acquire and retain their charges, and thus conduct the electric current by transporting these charges between the electrodes. It is assumed that the ions only are electrically active, since the electrolytic conductance is used as a measure of the ionic concentration. On account of the high electrical resistance of the solvent in the case of aqueous solutions, an almost negligible proportion of the total current carried is carried by the solvent. If ions resulting from the dissociation of molecules in aqueous solution are capable of acquiring energy in the form of electric charges, but in these solutions retain and transport this electrical energy only because of the dielectric property of the solvent, one might properly ask, What should we expect if solutes were dissolved and dissociated in a solvent which was in itself a conductor possessed of very low specific resistance? In such a case there seems to be no inherent reason why the mechanism of solution and dissociation of the molecules of the solute into constituent parts bearing precisely the same atomic relations to the solvent, should differ essentially from that which holds when a solute is dissolved in a dielectric solvent. In case the solvent were a metal it would be obviously impossible for the products of ionic dissociation to retain electric charges; hence it would be clearly out of the question to call these products ions, so that we have suggested the term "ionoids" to indicate the products of ionic dissociation in solutions in which the solvent is a metal. The "ionoids" in metallic solutions, like the ions in aqueous solutions, constitute that portion of the solute which has undergone dissociation and which is electrolytically active. The result of this electrolytic activity of "ionoids," however, will manifest itself in a manner directly the reverse of that manifested in the behavior of ions, not because of any fundamental difference in the atomic relations existing between the "ionoids" or ions and the solvent, but because of the reverse

¹ *J. Iron and Steel Inst.*, 2, 223 (1899).

of the electrical properties of the solvents. In a metallic solution practically the whole of the conductance is through the solvent and undissociated solutes, while the "ionoids" which are electrolytically active tend, like ions, to acquire energy in the form of electric charges, but on account of the nature of the solvent retention of this energy is impossible and it is, in consequence, transformed and dissipated in the form of heat. Thus the electrical energy transformed into heat by the "ionoids" may be expressed in terms of specific resistance and consequently the ionic concentration in solid solution in metals may be determined by deducting from the total specific resistance that due to the solvent and undissociated solutes. Under the above conceptions the dissociation theory of solution would be just as applicable to solid solutions in metals as to aqueous solutions; although the phenomena, when the two solutions were subjected to a difference of potential at two points, would manifest themselves in opposite directions. The differences, however, in electrical behavior of the two solutions are due not to any fundamental difference in the atomic relations existing between solutes and solvent, but to the differences in the electrical properties of the solvents.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF MOLYBDENUM.

By JOHN H. MÜLLER.

Received July 21, 1915.

The purpose of the present investigation was to redetermine the atomic weight of molybdenum by the oxidation of pure metal. It will be recalled that as early as 1859 Dumas¹ oxidized the sulfide, reducing the resulting oxide in hydrogen to metal. The mean of six determinations was 95.942.

In 1868 Debray used the method of Dumas.² The trioxide, in this case, was purified by sublimation from platinum. The mean of three determinations was found to be 95.524. Later Rammelsberg,³ from a single experiment, obtained a result very close to that of Dumas.

In 1895 Seubert and Pollard⁴ determined the indirect ratio $2. \text{AgCl} : \text{MoO}_3$, subsequently reducing the trioxide to metal in hydrogen, with the result, $\text{Mo} = 96.006$.

Vandenberghe⁵ reduced the dibromide to metal and oxidized the latter to trioxide by means of nitric acid. The mean of five determinations by this procedure was 96.088.

¹ *Ann. Chem. Pharm.*, 105, 84, and 113, 23.

² *Compt. rend.*, 66, 734.

³ *Berlin. Monatsb.*, 1877, p. 574.

⁴ *Z. anorg. Chem.*, 8, 434 (1895).

⁵ "Acad. Roy. Belge Mem. couronnes T.," 56.

Reagents.

Water.—Ordinary distilled water of the laboratory was redistilled, first from alkaline permanganate, then from acid permanganate, and finally alone. A block-tin condenser and well-seasoned Jena glass receivers were used.

Hydrogen Chloride.—This gas was prepared by the action of concentrated sulfuric acid upon concentrated hydrochloric acid and dried by passage through four wash bottles containing freshly dehydrated sulfuric acid. All connections were either fused or ground glass.

Ammonia.—This was prepared by warming ordinary ammonia water and conducting the gas through a double splash trap to an inverted large funnel, under which was placed a platinum dish containing water.

Hydrogen.—The hydrogen was obtained by electrolysis of 20% solution of caustic soda. Both electrodes were of pure nickel, while the generator of two liter capacity was so constructed that the inner compartment was entirely of glass—the wires being sealed in. The exit tube from the electrolytic cell was ground to fit the drying apparatus and was held in place by an external band of rubber. All other joints throughout the entire washing and drying system were fused. A current of five amperes furnished the maximum flow of gas. The latter was passed in turn through the following: silver nitrate, alkaline permanganate, concentrated sulfuric acid, broken caustic potash, a heated tube containing palladium asbestos, concentrated solution of caustic potash, concentrated sulfuric acid, drying tower (beads and sulfuric acid), soda lime and caustic potash tower, and phosphorus pentoxide.

Oxygen.—This gas was produced electrolytically from sodium hydroxide solution from an independent cell so as to take off the gas only from the inner compartment. The generator was the same as that used for the preparation of hydrogen, with the omission of the palladium asbestos tube. The oxygen was washed and dried as described under hydrogen.

Air.—The air was washed and dried by passing it through: (a) Silver nitrate and moist silver oxide; (b) 1-1 solution of caustic potash; (c) concentrated sulfuric acid; (d) concentrated sulfuric acid (tower and beads); (e) broken stick potash and soda lime; (f) phosphorus pentoxide.

Preparation of Molybdic Oxide.—500 g. of commercial molybdic oxide were converted to ammonium molybdate and treated with a little ammonium sulfide, filtered and evaporated to crystallization. The crude salt was recrystallized five times in large porcelain vessels. The resulting product was ignited to oxide and subjected to volatilization in hydrochloric acid gas. This was done without regard to temperature regulation. The first and last portions of the sublimate were discarded, the intermediate product being converted into ammonium molybdate. Large platinum dishes were the containing vessels. After evaporation of the

ammoniacal solution to dryness, the residue was transferred to quartz dishes and therein ignited.

The oxide thus obtained was placed in large quartz boats in a wide bore quartz tube and subjected to a fractional sublimation in air—at a temperature just below the fusing point, the crystalline sublimate being continuously removed from the quartz tube. About one-half of the oxide was sublimed from each charge, the remaining portions being discarded. It was noticed that the boats and a narrow strip of the quartz tube beneath the boats were superficially etched by the long-continued heating—due possibly to a small quantity of alkali present in the oxide. A portion of the sublimate, however, showed no tendency to etch a fresh boat even after twenty hours' ignition at a slightly higher temperature than that of the original sublimation. From 65 g. of oxide 45 g. of sublimate were obtained and constituted the starting product for a more careful fractionation in hydrochloric acid gas. The sublimation of molybdenum hydroxychloride was carried out in the apparatus shown in Fig. I.

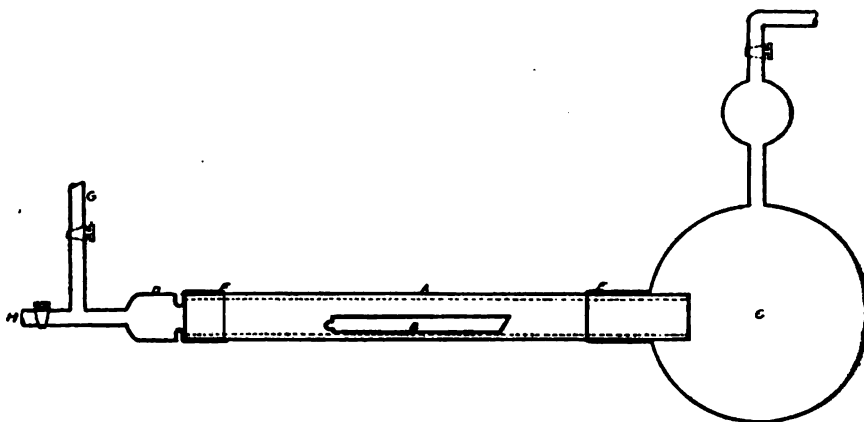


Fig. I.

- A. Quartz tube 2 cm. diam., length 80 cm.
- B. Large quartz boat.
- C. $\frac{1}{2}$ L. jena glass bulb.
- D. Adapter ground to fit A, held in place by external band of rubber at F.
- G. Entrance for dry air.
- H. Entrance for dry HCl.

The temperature was not allowed to exceed 250° throughout the operation. A slow current of dry air was first passed in at G to expel all traces of moisture, after which precaution it was possible to sublime large quantities of the oxychloride with no stoppage of the quartz tube. In the absence of all moisture, the very bulky sublimate showed no tendency to stick to the sides of the receiving bulb so that after removal of the excess of hydrogen chloride by dry air the contents of C could be almost

completely shaken out into a quartz beaker. To avoid the taking of alkali from the Jena glass bulb, washing was omitted. The sublimate was dissolved in water and the aqueous solution transferred from the quartz vessels to ammonia water contained in platinum dishes. After evaporation to dryness the residue was ignited to oxide in vessels of quartz.

The sublimation above described was repeated four times, each operation removing smaller residues of unsublimed oxide, the last portion leaving no weighable residue after heating to 200° in HCl. The final fraction of molybdenum trioxide thus obtained was resublimed in hydrochloric acid gas, dividing it into thirds. These three portions, upon conversion to metal, constituted Fractions I, II and III, used in determining the ratio of metal to oxide.

Metallic Molybdenum.—The molybdic oxide prepared as above was reduced to metal in quartz boats. A preliminary reduction was found quite necessary because an appreciable quantity of oxide in the final reduction led to the condensation of water in the vacuum apparatus, manometer tubes, etc. Its removal was difficult and time consuming.

The writer wishes to lay particular stress on the fact that the physical condition of the metal had much to do with the ease or the difficulty with which subsequent oxidation could be carried out. A very porous, finely divided material could not be obtained from the pure oxide after the latter was ignited at a temperature high enough to cause much crystallization, but if the ammoniacal solution of the hydroxychloride was only very gently ignited so as to expel only the excess of ammonium chloride—the non-crystalline residue could be very slowly reduced with the production of metal offering maximum surface and facilitating complete oxidation. The metal obtained as outlined above was preserved in a desiccator. It was used in the following determinations: (Fractions I, II and III.) The combustion furnace K, Fig. II, was constructed of

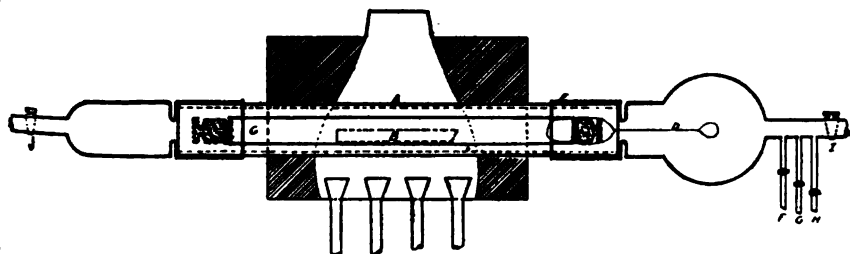


Fig. II.

asbestos, covered externally with sheet iron. A battery of special burners developed a temperature within the quartz core of more than 1000° . The furnace was cut longitudinally in equal parts so that it could be removed from the stationary quartz tube while the latter was at white heat,

This saved much time in cooling the charge and minimized error from leakage of air into the evacuated tube during the process of cooling to room temperature. The special advantage of a quartz tube here was evident as cold water could be applied to the hot tube immediately after removing the furnace sections, effecting a cooling to room temperature in a short time.

Apparatus for Reduction.—The apparatus used in the final production of metal was arranged as in Fig. II, A, a thick-walled quartz tube 90 cm. in length, internal diameter about 2 cm., into which was placed the bottling tube of clear quartz, C, containing boat B and metal. The quartz stoppers were pushed into place before removing the inner tube for transference of boat to weighing tube. Connections at J and E were ground and strong external bands of rubber were used to hold the glass adapters in close contact with the quartz tube. F was connected with a manometer to an air pump, H, to air apparatus, I, to a sulfuric acid trap for the exit of hydrogen current. The glass stopcocks at F, G, H, I, and J were all carefully reground with the finest procurable emery dust and were lubricated with metaphosphoric acid. No measurable leakage into the vacuum was noticed after one-half hour's standing, this test being applied before each reduction was carried out.

The use of a vacuum pump in the reduction of the metal served two purposes: first, the rapid and complete removal of air before each heating of metal to constant weight—as pure, dry hydrogen could be slowly admitted at J and the washing of the contents of the tube in this gas be carried out several times before applying heat; secondly, the subsequent cooling of the metal was effected *in vacuo* and the cooled metal then washed in dry air admitted at H before the bottling tube was removed by the platinum wire D.



Fig. III.

- A. Thick-walled transparent quartz tube, length 20 cm., inner diam. 15 mm., weight 32 grams.
- B. Quartz boat containing metal.
- C. Capillary tube length 14 cm., ground cap at F.
End of tube at D ground inside to fit stopper E and outside beveled to fit oxygen apparatus.

Weighing Tube and Counterpoise.—Weighing tube and counterpoise shown in Fig. III were almost identical in weight and shape, the weight of the latter being brought to within a milligram of the former by the introduction of a small quartz rod.

Apparatus for Oxidation.—Arranged as in Fig. IV. The entire apparatus was protected from dust by enclosure in a large glass compartment with a narrow opening at the top to permit the escape of heat.

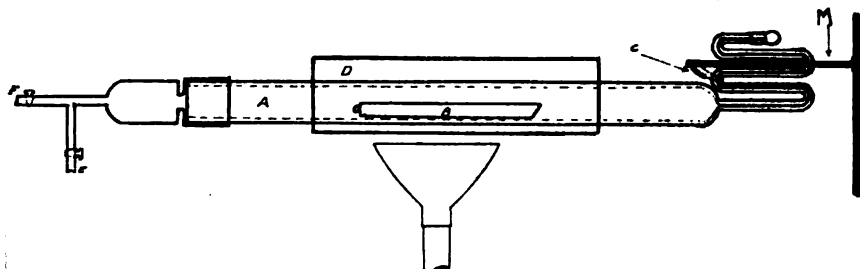


Fig. IV.

- A. Quartz weighing tube boat at B.
 C. Platinum wire and spring to hold A in place.
 E and F. Air and oxygen.
 D. Quartz jacket tube to protect A from direct flame.
 M. Fork to hold platinum wire.

All of apparatus shown in figure was enclosed in a large glass chamber to avoid dust.

Balance and Weights.—The balance used was a Troemner No. 10; sensibility factor, 0.00022 g. Weights, gold plated, were calibrated by Richard's substitution method. No rider was used. To eliminate small errors in weighing from static charges upon the quartz weighing tubes some highly radioactive residues were placed within the balance case. It was observed that quartz possesses the property of holding a static charge to a degree far surpassing that of glass, and weighings carried out without the aid of radioactive material were only satisfactory after a period of several hours for the establishment of equilibrium. The above-mentioned material lessened the time required for weighing and eliminated troublesome irregularities which could only be traced to charges upon the quartz apparatus. Forefinger and thumb stalls of lint free linen much facilitated the manipulation of weighing tube and counterpoise and were found much more convenient than either tongs or handkerchief.

Specific Gravity of Metal and Trioxide.

The means of three determinations for both metal and trioxide were used for vacuum corrections. Pure toluene, freshly distilled over sodium at 110°, was selected for the determination, previous experiment having established the complete unalterability of metal and oxide in this liquid.

Mo.		MoO ₃ .	
D ₄ ²⁶	(a) 10.270	D ₄ ²⁶	4.659
D ₄ ²⁶	(b) 10.296	D ₄ ²⁶	4.669
D ₄ ²⁶	(c) 10.278	D ₄ ²⁶	4.760
Mean,	10.281	Mean,	4.696
Ratio Mo : MoO ₃ .			

FRACTION I.

Mo taken in <i>vacuo</i> .	Total number of hours heating in hydrogen at 1000°.	MoO ₃ found in <i>vacuo</i> .	Atomic weight.
(a) 0.52591	25	0.78879	96.027
(b) 0.56327	20	0.84487	96.012
(c) 1.12757	24	1.69117	96.031

FRACTION II.

(a) 0.53014	21	0.79517	96.014
(b) 1.10754	20	1.66130	96.002
(c) 1.62166	21	2.43181	96.080
(d) 1.45530	22	2.18259	96.047

FRACTION III.

(a) 0.94968	18	1.42428	96.048
(b) 0.65659	20	0.9870	96.054

Mean, 96.035

Mean omitting (c) Fraction II, 96.029

In the first three of the above determinations (Fraction I), the metal was heated in hydrogen for periods of about six hours each and required four weighings to obtain constant weight (error ± 0.00002). In the later determinations the time of ignition was extended to over seven hours in hydrogen and averaged three weighings to secure constant weight within the same limit of error. Preceding each reheating, all air was removed by evacuating the tube—refilling the vacuum several times with hydrogen (stopcocks J and G, Fig. II).

After ignition the sectional furnace K was removed—the tube again evacuated while still hot. After complete cooling had taken place, the vacuum was refilled by a current of air through (H), several operations insuring the removal of all traces of hydrogen.

The bottling tube C, Fig. II, was closed before removal from the ignition tube and the transference of the boat to weighing tube (Fig. III) effected by bringing the ground end of C to the open end of the weighing tube, pushing the boat into place with a quartz rod. Tube and counterpoise were desiccated over phosphorus pentoxide twelve hours before weighing. The oxidation of the metal was carried out as shown in Fig. IV. Heating in a very slow current of air was continued until nearly all of the metal was oxidized. The stopcock E was then closed, admitting oxygen at F to complete the operation at a more elevated temperature. The quartz jacket D served to protect the weighing tube from direct heating and also to secure a more uniform temperature for the tube and contents.

The temperature was regulated so as to avoid all signs of sintering of the oxide and at no time was high enough to cause more than a slight volatilization of the oxide above the boat. The weighing tube A was

held in the ground adapter F by the platinum wire and spiral springs at C. As the initial heatings in air and oxygen were carried out at the lowest reacting temperature, the time required to complete the oxidation was nearly as great as that expended in the reduction to metal, averaging about fifteen hours.

It will be noticed that the result of determination C, Fraction II, is considerably higher than the other values obtained, which can probably be explained by the fact that the boat was in this instance taxed to its limit of capacity—the metal requiring an abnormally long series of heatings in oxygen to constant weight while some doubt was entertained as to the complete reduction of this larger quantity of metal. In view of the above considerations, the writer feels justified in selecting the mean of the eight more concordant results (96.029) as the most probable value.

The practically perfect condition of the quartz boat and weighing tube after all of the above determinations—representing about 190 hours in hydrogen at 1000° for the former and about 150 hours for both tube and boat in air and oxygen near the subliming point of oxide, proved conclusively that metallic molybdenum and its oxides have no effect on quartz through a wide temperature range. This fact is of interest as other more commonly used substances, porcelain and platinum in particular, are very decidedly affected under like circumstances.

Effort was made to prepare molybdic acid without using quartz or platinum vessels, but the product obtained could not be subsequently sublimed in quartz without a decided etching of the boat and tube. Several samples of supposedly pure oxide from different sources likewise showed a noticeable effect upon quartz when an air sublimation was attempted. Hence, it was concluded that the etching in the above mentioned cases must be laid to the presence of small quantities of alkali and not to any action of molybdenum or its oxides. Possible error from volatilization of the oxide during the long periods of heating in air and oxygen seemed to have been entirely obviated by the special construction of the weighing tube (Fig. III).

Preliminary experiments were made to establish this—using a temperature much higher than that used in the actual determinations—all of the oxide having been driven out of the boat into the weighing tube to a point close to the capillary without loss in weight.

Behavior of Metallic Molybdenum in Hydrogen.

The possible absorption of hydrogen by metallic molybdenum and consequent source of error was investigated through a range of temperature from 0° to 600°, fixing the pressure at 0.5 mm. and plotting weight against temperature.

The apparatus used was similar to that shown in Fig. II, less the furnace K and the inner tube C. The heavy quartz tube A was

surrounded by an asbestos covered metal jacket furnished with a pyrometer. Approximately three grams of molybdenum were introduced into the weighing tube (Fig. III) which was then sealed off at the wide end, leaving open only the capillary C. The weighing tube containing metal was now introduced into the quartz ignition tube and the apparatus then evacuated, refilling repeatedly with hydrogen to expel all air. The tube was then raised to red heat for seven hours and finally cooled to room temperature in hydrogen. The initial weighing was taken after evacuation of the hydrogen at 20° and replacement of the latter by air. A series of weighings were then made, fixing the pressure in hydrogen at 5 mm. and cooling to room temperature at this pressure in hydrogen before replacing the latter by air.

Cooled from	Pressure in hydrogen. Mm.	Weight of metal in grams.
20° to 0°	760	3.31980
50° to 20°	760	3.31981
100° to 20°	0.5	3.31994
200° to 20°	0.5	3.32001
360° to 20°	0.5	3.31997
500° to 20°	0.5	3.31991
580° to 20°	0.5	3.31988

From these results it was concluded that any error due to absorption of hydrogen by the metal was negligible and that the evacuation of tube and replacement of hydrogen by dry air, as carried out in all of the determinations of the ratio of metal to oxide, accomplished the complete removal of hydrogen from the metal.

Conclusion.

In concluding, it may be stated that the method used in the preceding experiments for determining the ratio of molybdenum to its trioxide differs from other investigations of the same ratio in the following essentials:

1. The purification of materials was greatly aided by the use of pure quartz apparatus which proved to be quite unaffected by molybdenum and its oxides.
2. Provision was made for complete prevention of loss of molybdenum oxide by volatilization.
3. An air sublimation of the trioxide in quartz and the fractionation of molybdenum hydroxychloride to constant composition under carefully regulated temperature conditions to insure complete absence of tungsten.
4. A protracted preliminary reduction of the oxide in large boats offering maximum surface for complete removal of oxygen, and, finally, the choice of an oxidation of the metal in place of the reduction of the weighed oxide, made possible through the use of the quartz bottling apparatus together with the construction of a weighing tube to prevent loss of oxide.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY,
No. 254.]

THE DENSITIES AND DEGREES OF DISSOCIATION OF THE SATURATED VAPOR OF PHOSPHORUS PENTACHLORIDE.

BY ALEXANDER SMITH AND ROBERT H. LOMBARD.

Received July 19, 1915.

The vapor densities of phosphorus pentachloride have been studied by Mitscherlich¹ (one observation) and by Cahours² at atmospheric pressure. Wurtz³ and Troost and Hautefeuille⁴ made measurements at reduced pressures, the former mixing the vapor with air for the purpose. Wurtz⁵ also studied the effect of excess of phosphorus trichloride on the densities. All these results have been studied in an instructive manner by Willard Gibbs,⁶ and the last set also by Wegscheider.⁷ Recently Carl Holland,⁸ working under Nernst, has published additional measurements which he uses to obtain a general formula and to calculate the heat of reaction. His observations and the results calculated by him from them, however, are not in harmony. Thus, from the first series of four observations, he deduces the following values for α , namely 0.214, 0.740, 0.850, 0.978. Our calculation from the same data shows that the values should be 0.243, 0.752, 0.855, 0.975. If the observed value of d (see below) in the first observation had been 494 instead of 464, the value 0.214 would have been correct. Again, Holland defines $\log K$ for acetic acid vapor as $\log \frac{[(CH_3COOH)_2]}{[CH_3COOH]^2}$. The corresponding formula for the

pentachloride is not given, and no particulars as to the units employed in expressing the concentrations for either substance are to be found in the paper. In the dissertation, however, for the loan of which we are indebted to the Librarian of Yale University, Holland states that for acetic acid $K = \frac{(p-d)^2}{d RT 760}$, where p is the observed pressure and d

is the difference between the observed pressure and that which would have been exercised if, on cooling from a temperature at which dissociation was complete, only the laws of Boyle and Charles had been in operation and no combination had taken place. Hence d represents the partial pressure of the PCl_5 molecules and $p-d$ the sum of the partial pressures of the two dissociation products. This formula is the inverse of the one

¹ *Pogg. Ann.*, 29, 221 (1833).

² *Compt. rend.*, 21, 625 (1845); *Ann. chim. phys.*, [3] 20, 369 (1847).

³ *Compt. rend.*, 76, 601 (1873).

⁴ *Ibid.*, 83, 977 (1876).

⁵ *Ibid.*, 76, 610 (1873).

⁶ *Am. J. Sci. and Arts.*, [3] 18, 381 (1879).

⁷ *Monatshfte Chem.*, 20, 307 (1899).

⁸ *Z. Elektrochem.*, 18, 235 (1912).

indicated in the paper. The values of $\log K$ given in Holland's table, however, are entirely different from those which we obtain by substituting his data in the above formula, after adapting it to the case of the pentachloride by substituting $\{(p-d)/2\}^2$ for $(p-d)^2$. Thus, taking the first set of four observations, and assuming $R = 0.0821$, we obtain for $\log K$: $\bar{3}.22239$, $\bar{2}.67977$, $\bar{1}.02926$, $\bar{1}.91442$, while Holland gives the values $\bar{1}.91668$, $\bar{2}.44032$, $\bar{2}.09091$,¹ $\bar{4}.96885$. His values, indeed, diminish progressively while ours increase. Using $p-d$ as the numerator yields, naturally, no better correspondence. Employing the same formula inverted leaves the numbers still wholly discordant. With the formula

$$K = \frac{dRT}{\{(p-d)/2\}^2}, \text{ which corresponds with the inverted form in the published paper, but omits the correction to atmospheres, we obtain from the}$$

same four sets of data the following values for $\log K$: $\bar{1}.89680$, $\bar{2}.43942$, $\bar{2}.08993$, $\bar{3}.20477$. The first three results now agree fairly well with Holland's, but the fourth does not. If in calculating the fourth result we employ the temperature on the centigrade scale, 340°C. instead of 613°abs. , we obtain $\log K = \bar{4}.94879$, which is much closer to Holland's value. The remaining seven values of $\log K$ are all incorrect, but, being too great, cannot be explained in the same way as the fourth. The fifth should be 0.24661 instead of 0.47643 . Here, if the value of p in the sixth observation, namely 1779.0 had been used by mistake instead of the value of d (1029.3) in the numerator only, the $\log K$ would become 0.48424 , which is nearer to his value. Apparently this was the formula employed, although with some inconsistency, the basis of which we have not succeeded in determining. Employment of his incorrect values of α does not remove the inconsistency. Dr. Calvert and Professor C. M. Carson have both been kind enough to make the calculations independently and their results agree with ours.

In the dissertation (p. 25) Holland states that the eleven sets of data given were chosen from a large number, and were selected on account of the fact that they were very consistent. The confusion in his figures raises the question whether, after all, he did make the best selection, as well as the question whether it is ever advisable to publish only those results which appear to be favorable. It is worth noticing also that the temperatures, which reach as high as 358° , were determined with a mercury thermometer. There are also numerous misprints (Gay-Cassac for Gay-Lussac, 462° abs. for 465° abs., etc.). Then, too, the same symbol is used for different things and different symbols for the same thing. Thus, on p. 24, in line 1, he employs p for the total observed pressure while in line 5 it is equivalent to the partial pressure of the associated molecules. Again, on p. 23, line 2 from below, he defines P as the pressure calculated for no

¹ In the published paper, this value is given as $\bar{1}.09091$.

reaction—that is, no association on cooling. But on the same page, he gives the formula $K = \frac{4P(\delta - \Delta)^2}{(2\Delta - \delta)\delta}$, which is correct only if P is the total observed pressure (one of the senses in which p was employed). He also gives $K^1 = \frac{Px^2}{1 - x^2}$, where x is a misprint for α used in the table,

and the formula is correct only provided P is the total observed pressure.

All the published observations mentioned above refer to the unsaturated vapor. The present measurements concern the saturated vapor, in equilibrium with the solid phase.

The Apparatus.—The bath and thermometer were the same as in the study of the ammonium halides,¹ except that paraffin was used as the bath-liquid. The bulb was modified. The phosphorus pentachloride was placed in bulb A (Fig. 1). The bottom of this bulb was blown very

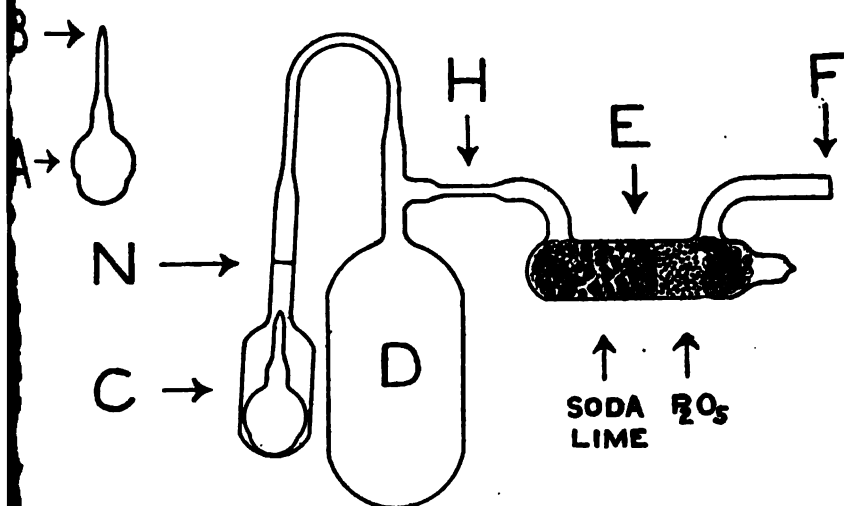


Fig. 1.—Vapor Density Bulb.

thin to facilitate subsequent breaking. After being filled, the neck was drawn out to a capillary, about half of the substance was distilled out, and the capillary was sealed at B. This distillation removed impurities, such as the trichloride and oxychloride of phosphorus, chlorine, and phosphorus, which might have been present. The charged bulb was then cleaned and enclosed in the bulb C, and the latter was attached at N to the vapor density bulb D. The drying tube E contained soda-lime and phosphorus pentoxide. The apparatus, with the exception of the part containing the drying agents, was then warmed with a Bunsen flame to drive off moisture adhering to the inner surface of the glass. When cold,

¹ Smith and Lombard, *THIS JOURNAL*, 37, 38 (1915).

it was sealed at F. After lying in this condition twenty-four hours, the bulb containing the pentachloride was broken by shaking the apparatus. The tube was then opened at F, sealed at that point on to the pump, evacuated to 0.1 mm., and finally sealed off from the pump at H. The heating and pentoxide ensured the absence of moisture when the pentachloride bulb was broken, and the pentoxide prevented access of moisture while the bulb was being sealed to the pump. The soda-lime was used to prevent chlorine or hydrogen chloride from entering the pump.

TABLE I.—DENSITIES OF PCl_5 VAPOR (SATURATED)—DATA.

	G. PCl_5 in large bulb.	Vol. cc. large bulb.	Vapor dens. G. per cc.	Deviation from mean.	Vapor dens. Moles per L.
90°	0.0117	59.29	0.000197	00	0.000945
	0.0145	73.74	0.000196	— 1	0.000942
	0.0126	61.76	0.000204	+ 7	0.000980
	0.0135	70.66	0.000190	— 7	0.000914
Average vapor density.....			0.000197 ± 2 , or $\pm 1.0\%$		0.000945
100°	0.0279	84.08	0.000332	00	0.00159
	0.0293	87.06	0.000337	+ 5	0.00162
	0.0245	74.08	0.000331	— 1	0.00159
	0.0236	73.72	0.000320	— 12	0.00154
	0.0283	83.87	0.000338	+ 6	0.00162
Average vapor density.....			0.000332 ± 2 , or 0.6%		0.00159
110°	0.0320	55.86	0.000573	+ 4	0.00275
	0.0490	87.06	0.000563	— 6	0.00270
	0.0485	85.19	0.000569	00	0.00273
	0.0420	73.72	0.000570	+ 1	0.00274
Average vapor density.....			0.000569 ± 1 , or 0.2%		0.00273
120°	0.0575	61.67	0.000933	+ 4	0.00448
	0.0603	65.07	0.000927	— 2	0.00445
	0.0781	84.29	0.000927	— 2	0.00445
	0.0589	63.50	0.000928	00	0.00446
Average vapor density.....			0.000929 ± 0.5 , or $\pm 0.1\%$		0.00446
140°	0.1737	74.39	0.002335	+ 59	0.01121
	0.1484	63.59	0.002333	+ 47	0.01120
	0.1658	77.91	0.002129	— 157	0.01022
	0.1617	68.88	0.002348	+ 62	0.01127
Average vapor density.....			0.002286 ± 41 , or $\pm 1.8\%$		0.01098
150°	0.2874	84.55	0.003399	— 49	0.01632
	0.3021	87.02	0.003471	+ 23	0.01666
	0.2473	70.93	0.003487	+ 39	0.01674
	0.2547	73.83	0.003450	+ 2	0.01656
	0.2550	74.27	0.003433	— 15	0.01648
Average vapor density.....			0.003448 ± 12 , or $\pm 0.35\%$		0.01655
160°	0.3110	65.24	0.004767	— 166	0.02288
	0.4029	81.00	0.004974	+ 41	0.02388
	0.4264	84.28	0.005059	+ 126	0.02429
Average vapor density.....			0.004933 ± 64 , or $\pm 1.3\%$		0.02368

The Data.—As the vapor pressure of phosphorus pentachloride reaches 60 mm. at 162.8° , the measurements extended from 160° down to 90° . Since immersion in the bath for 45 and 25 minutes at 100° gave identical results, the period of immersion was 25 minutes at all the other temperatures. The weight of phosphorus pentachloride in the large bulb (Col. 2) was determined by precipitating the chlorine as silver chloride. The method of calculating the results was the same as that used by us in the case of the ammonium halides.¹

In Table II the results are summarized. The dissociation pressures (Col. 7) are those determined by Smith and Calvert,² and the values at

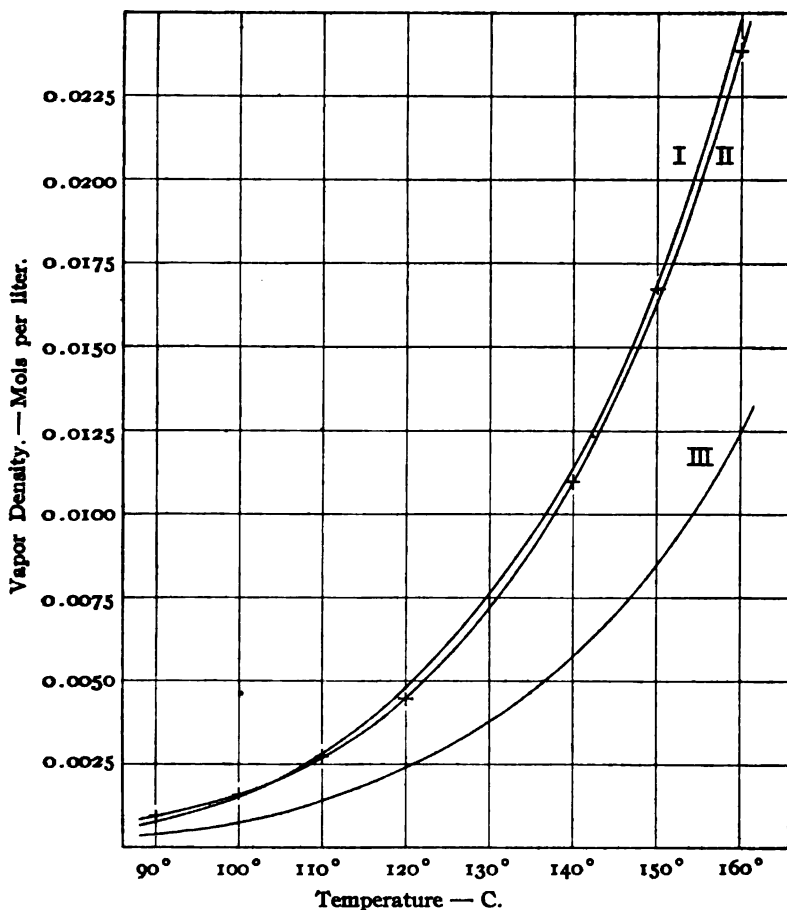


Fig. 2.—Density of Saturated Phosphorus Pentachloride Vapor. Curve I: Undissociated (calculated). Curve II: Observed. Curve III: Completely Dissociated (calculated).

¹ *Loc. cit.*

² *THIS JOURNAL*, 36, 1363 (1914).

90° and 100° are correct ± 3 mm. and at the higher temperatures ± 5 mm. For the purpose of comparison, the densities which the vapor would possess if it were undissociated (Col. 5) and completely dissociated (Col. 6), and yet exercised the measured dissociation pressures, are given. To show the relationship between the observed vapor densities and those calculated for no dissociation and for complete dissociation the values are plotted in Fig. 2. It will be seen that the curve of observed values lies close to that calculated for the densities of the undissociated substance. Above 100° the curves are practically parallel, showing that the effect of higher temperatures in increasing the degree of dissociation is almost exactly counterbalanced by the effect of the higher dissociation pressures in inhibiting dissociation.

TABLE II.—DENSITIES OF PCl_5 VAPOR (SATURATED)—SUMMARY.
Vapor density.

Temp.		Observed (Δ).		Calculated.		Dissoc. press. mm.
C.	Abs.	G. per cc.	Mols per L.	Undissoc. Mols per L.	Compl. dissoc. Mols per L.	
90	363	0.000197	0.000945	0.000795	0.000398	18
100	373	0.000332	0.00159	0.001505	0.000753	35
110	383	0.000569	0.00273	0.00281	0.00140	67
120	393	0.000929	0.00446	0.00477	0.00239	117
130	403	0.00760	0.00380	191
140	413	0.002286	0.01098	0.01142	0.00571	294
150	423	0.003448	0.01655	0.01688	0.00844	445
160	433	0.004933	0.02368	0.02481	0.01241	670

The percentage dissociation of the saturated vapors, calculated from the data in Table II, is given in Table III.

TABLE III.— PCl_5 , PERCENTAGE DISSOCIATED— α .

Temp.	90°.	100°.	110°.	120°.	130°.	140°.	150°.	160°.
Percentage...	apparently assoc.	apparently assoc.	2.8	7.1	...	4.0	2.0	4.8

Even if we assume an error of -3 mm. in the dissociation pressure at 90°, and use the maximum value, 21 mm., the vapor density of the undissociated substance would be 0.000927 moles per liter, or slightly less than the value found. There appears therefore to be a slight degree of association at 90° and possibly at 100°.

On account of the form of the relation between the density and the value of α , a very slight error in the former produces a large divergence in the latter. The results, therefore, although irregular, are not inconsistent with the estimated accuracy of the measurements, involving a limit of error of from 0.1 to 1.8%.

General Formula for the Dissociation Pressures.—A Kirchoff-Rankin-Dupré equation for the dissociation pressures, based on three points (160°, 670 mm; 140°, 294 mm; 108.2°, 60 mm.) was computed: $\log P = -6724.22/T - 19.1978 \log T + 68.9701$. This formula represents the

pressures up to 160° with a divergence of not more than 5 mm. (see Table IV).

TABLE IV.—OBSERVED AND CALCULATED PRESSURES—PCl₅.

Temp.	Pressure.			Temp.	Pressure.		
	S. & C.	Calc.	Diff.		S. & C.	Calc.	Diff.
90.0	18	20	+2	140.0	294	294
98.1	31	33	+2	150.0	445	450	+ 5
108.2	60	60	...	157.7	608	612	+ 4
120.0	117	113	-4	160.0	670	670	..
133.0	219	214	-5	162.8	760	745	-15

Latent Heat of Vaporization.—With the assistance of the above equation, the molar latent heat of vaporization was calculated by the method used in the case of the ammonium halides. The Clausius-Clapeyron equation, with the values inserted, is as follows:

$$L = T \frac{P}{760} \left[\frac{6724}{0.4343 T^2} - \frac{19.20}{T} \right] \frac{0.02419}{\Delta m} \text{ Kg. cal.}$$

The molar heats of vaporization are given in Table V.

TABLE V.—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

Temp.	90°.	100°.	110°.	120°.	140°.	150°.	160°.
Lat. heat.....	14.2	15.6	16.6	16.9	15.6	14.9	14.9
Average value 15.5 \pm 0.28, or \pm 1.8%.							

The observed values of the degrees of dissociation were too small and too irregular to permit of the calculation of the heat of dissociation. It is evident, however, that the value is negative, *i. e.*, heat is absorbed by the dissociation of the saturated vapor.

Note on the Previous Results with Ammonium Iodide.—It will be recalled that below 345° the vapor of this substance was found to be in part associated and above 345° but little dissociated. That no secondary reaction was responsible for this result was shown by the fact that when the bulbs were opened under water, no permanent gas, such as nitrogen or hydrogen, was found.¹ A colleague has suggested that a soluble gas, such as hydrogen iodide or ammonia might have been present. Although it is not clear to us how this could have occurred, without the simultaneous presence of an insoluble gas, nevertheless it seemed worth while to settle the question by a decisive experiment. Two vapor density-bulbs (60–75 cc. capacity, with attached small bulb), similar to those used in the published experiments, were used. Ammonium iodide was placed in the small bulb. After evacuation and sealing, they were kept for 30 minutes, one at 330°, and the other at 340°. To avoid the risk of cracking, they were removed from the bath without being sealed apart. When opened under mercury, they filled up at once and only a small bubble of gas (estimated by comparison with a buret to be not over 0.3 cc.) remained.

¹ *Loc. cit.*, p. 107.

This was undoubtedly the air not originally removed by the pump and absorbed air liberated from the surface of the salt and of the glass by the heating. The original conclusion, that ammonium iodide in the state of saturated vapor is in part associated, is therefore undoubtedly correct.

Summary.

1. The vapor densities of the saturated vapor of phosphorus pentachloride were determined from 90° to 160° .
2. The degrees of dissociation calculated from the vapor densities show that the saturated vapor is somewhat associated at 90° , and dissociated to an approximately constant extent of about 4% from 110° to 160° .
3. The latent heat of vaporization was calculated to be 15.5 Kg. cal. per mol.
4. A note on the case of ammonium iodide, previously investigated is appended.

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NOTES.

A Convenient Weighing Pipet.—Recent work the author has made necessary the extensive use of a weighing pipet. One of the type suggested by Mertes¹ was first adopted, but was found to have the following disadvantages:

1. It is inconvenient to fill and difficult to clean.
2. The necessary size of the tubing for the neck to permit of its being hung on the balance, made the larger sizes too fragile.

To remove these defects the form shown in Fig. 1 was devised. It consists essentially of an ordinary pipet body fitted with a stopcock at the bottom and a short neck of thick-walled narrow glass tubing with a bulb, A, blown in it. The purpose of this latter is two-fold: first, to serve as an overflow bulb when filling, and second, to serve as a means of support by preventing the neck from slipping through the supporting hook B, which hangs from the balance arm. The supporting hook is made out of some sheet metal, such as brass, about one millimeter thick. Two elevations of the latter, front B, and side C, are shown. The bulb E is cut slightly wider than the diameter of the

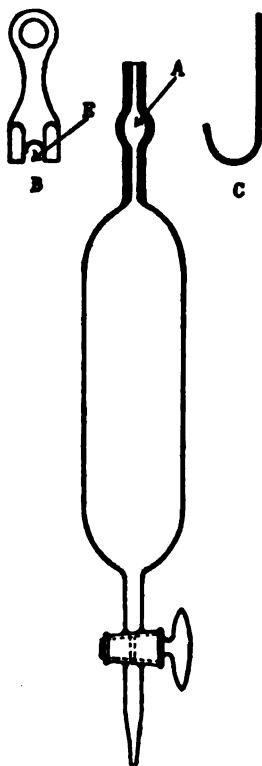


Fig. 1.

¹ *J. Ind. Eng. Chem.*, 7, 236 (1915).

neck of the pipet so as to admit the latter freely, and yet not wide enough to allow the bulb A to slide through.

A series of such pipets of varying capacities, having the same sized neck, may be constructed and thus used with the same hook. For use with quantities less than their total capacity the larger pipets may be graduated to indicate every 5 cc. or so. For use with more volatile liquids ground glass caps may easily be fitted both to the top and bottom to prevent possible evaporation. Anyone having a little skill at glass-blowing can construct this type of pipet, and to make its construction still more simple it can be made from the body of an ordinary plain pipet.

The advantages of this form of pipet can readily be seen; it is easily filled and cleaned, and its compactness permits its being conveniently weighed on the ordinary analytical balance. Furthermore, its lack of fragility reduces the probability of breakage.

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Note on the Interpretation of Molecular Weight Results from Measurements on Solutions (with special reference to a paper by Beckmann and Maxim).—In a recent memoir,¹ Beckman and Maxim record some measurements of the molecular weight of phenol which were made in order to test the influence both of temperature and the nature of the solvent.

Two solvents were employed, carbon tetrachloride and bromoform, the former at four different temperatures, namely -23° , $+75.4^{\circ}$, $+66.3^{\circ}$ and $+54.1^{\circ}$, the latter only at its freezing point ($+8^{\circ}$).

In all cases, phenol was found to be associated, the degree of association increasing continuously over the whole range of concentration tested, being about 1.0 in very dilute solution and exceeding 3 in the strongest solutions in freezing carbon tetrachloride.

From the comparison of the degree of association at the same concentrations in carbon tetrachloride the conclusion was drawn that, at any rate between 75.4° and 54.1° , alteration of temperature has but little effect on the molecular weight of phenol. At -23° (freezing carbon tetrachloride) the degree of association is distinctly greater than at 75° , but, even so, variation of temperature was held to be much less effective in altering the molecular size than variation of concentration.

The interpretations given by Beckmann and Maxim of their results seem to the writer somewhat inadequate. It may be pointed out that, in the measurements of Beckmann and Maxim (as in all similar measurements), the actual effect of temperature cannot be ascertained until a second factor is accounted for, namely, the variation of the dielectric constant of the solvent with the temperature; for, the influence of the

¹ *Z. physik. Chem.*, 89, 411 (1915).

nature of the solvent can in a large measure be correlated with the magnitude of its dielectric constant,¹ the degree of association being greater the lower the dielectric constant.

Now as the dielectric constant diminishes with rise of temperature, the two factors, namely, increase of temperature (tending to produce dissociation) and decrease of dielectric constant (permitting an increased degree of association), serve in some measure to counterbalance one another. No measurement appears yet to have been made of the variation with temperature of the dielectric constant of carbon tetrachloride, so that the true effect of temperature in reducing the degree of association cannot be ascertained. It will, undoubtedly, be greater than Beckmann and Maxim conceive.

Although not indicated by Beckmann and Maxim, their results are in harmony with the rule that the higher the dielectric constant of the solvent the smaller the degree of association of the solute. The following figures illustrate this fact:

Solvent.	Dielectric constant.	Grams of phenol per 100 cc. solution.	Degree of association.
Carbon tetrachloride (23°)...	2.25 ₁₈ ²	2.50	2.85 ⁴
Bromoform (+8°).....	4.58 ₁₈ ²	2.50	1.16

The order is the same at other corresponding concentrations and is unchanged even if the results in boiling carbon tetrachloride be compared with those in freezing bromoform.

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An Allotropic Modification of Lead.—The existence of a gray allotropic modification of lead has recently been observed by Heller,⁵ who found that, when a piece of bright, pure lead was placed in a nitric acid solution of lead acetate, transition commenced at the end of two days and was complete at the end of about three weeks.

A similar phenomenon has been observed by the writer in an electrolysis experiment, which substantiates Heller's observation: The electrolyte employed in this experiment was nitric acid (sp. gr. 1.42), the cathode a piece of sheet lead 2 cm. wide, 2 mm. thick and 10 cm. long, and the anode a thin piece of platinum foil. A current of 2–3 amperes at 6 volts was passed through the electrolyte for eight hours, at the end of which time the current was stopped and the lead cathode removed immediately.

¹ Meldrum and Turner, *J. Chem. Soc.*, 93, 876 (1908); 94, 1605, 1805 (1910); Turner, *Ibid.*, 99, 880 (1911); 101, 1923 (1912); Turner and Pollard, *Ibid.*, 105, 173 (1914); Turner and Bissett, *Ibid.*, 105, 1777 (1914); Turner, "Molecular Association," Longmans, 1915.

² B. B. Turner, *Z. physik. Chem.*, 35, 385 (1900).

³ Canwood and W. E. S. Turner, *J. Chem. Soc.*, 104, 276 (1915).

⁴ Determined graphically from Beckmann and Maxim's data.

⁵ H. Heller, *Z. physik. Chem.*, 89, 761 (1915).

Examination showed that the portion of the lead cathode in the electrolyte had increased slightly in volume, and that it had lost its former malleability and firmness. Its bright color had changed to gray. On rubbing the lower part of the electrode between the fingers, it was found to have been completely transformed into small particles, which could be rubbed into a fine powder, or pressed together into a soft mass.

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July 17, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

THE RATE OF CONVERSION OF CINCHONINE INTO CINCHOTOXINE.¹

(ON CATALYSES WITH WEAK ACIDS. VI.)

By H. C. BIDDLE AND O. L. BRAUER.

Received June 19, 1915.

1. **Introduction.**—The most carefully investigated cases of catalysis in aqueous solution are those reactions of hydrolysis in which the accelerating influence of an acid is largely determined by the concentration of the hydrogen ions. Such, for example, are the familiar inversion of cane sugar and the saponification of an ester in the presence of an acid. In the case of the remarkable conversion of the cinchona alkaloids into their poisonous isomers in the presence of weak organic acids we are, however, dealing with a catalysis of a different nature. In this catalysis, as has been previously shown, the speed of the reaction is apparently a direct function of the molecular concentration of the undissociated acid and an inverse function of the concentration of the hydrogen ion.

The rate of the conversion of cinchonine to cinchotoxine was measured by Biddle and Rosenstein² for the alkaloid in two concentrations of acetic acid. In the present paper is given a detailed study of this catalysis in the presence of various acids through a wide range of concentration of the several acids studied and in mixtures of acetic acid and hydrochloric acid presenting also a wide range in concentration of H^+ ion. The data obtained in conjunction with like data from the study of the stereoisomeric cinchonidine and the two stereoisomers, quinine and quinidine, would, it was believed, afford a basis for a more thorough investigation of this extraordinary catalysis. Such data might naturally among other things be expected: first, to show with some greater degree of certainty not only what molecular species are involved in each reaction, but also

¹ Biddle, *Ber.*, 45, 526, 2832 (1912); *THIS JOURNAL*, 34, 500 (1912); 35, 273 (1913); 36, 84 (1914); Biddle and Rosenstein, *Ibid.*, 35, 418 (1913).

² *THIS JOURNAL*, 35, 418 (1913).

in what quantity each is concerned; second, to make clear to some extent the nature of the retarding influence of the hydrogen ion, as well as that of the accelerating influence of the organic acid; third, to furnish through a comparative study of the reaction velocities observed, some definite information regarding the influence of optical isomerism upon the speed of the conversion. As will be shown in a later article (the eighth in this series) on the nature of this catalysis, these expectations have been fully realized in the interpretation of the data presented in this paper and the following one on "The Rate of Conversion of Cinchonidine into Cinchotoxine."

2. The Method of Analysis.—In the separation of cinchotoxine from cinchonine, the method first used in these investigations¹ involved an extraction with ether and a subsequent dehydration of the ethereal solution, the cinchonine being difficultly soluble in dry ether. The method, however, in addition to the error due to a slight solubility of cinchonine in ether, presented experimental difficulties which rendered it somewhat objectionable. Of the two methods employed by Biddle and Rosenstein,² a gravimetric and a polarimetric, the latter proved so accurate and at the same time so expeditious that it was used by them largely in their determinations. In the present investigation³ this method is employed almost exclusively. The polarimetric method⁴ is based upon the fact that the rotatory power of solutions of cinchonine salts is much greater than that of the corresponding cinchotoxine salts. The change in the rotatory power of a solution of a cinchonine salt becomes, then, a measure of the extent to which change to cinchotoxine has taken place.

In view of the isomeric rearrangements which cinchonine and the cinchona alkaloids in general may undergo in the presence of excess of strong mineral acids,⁵ and the consequent effect that slight changes in these directions might exert upon the optical activity of the solution, it was necessary to compare the gravimetric and polarimetric methods of measuring the conversion of cinchonine to cinchotoxine to determine whether or not the results were strictly comparable. In a previous paper⁶ the optical method was checked with a gravimetric method depending on the solubility of cinchotoxine in ammonium salts. The reaction velocities as

¹ Biddle, *THIS JOURNAL*, 34, 504 (1912).

² *Ibid.*, 35, 418 (1913).

³ The greater portion of the experimental work presented in this paper was carried on at about the same time as that of Rosenstein and Biddle, the polarimetric method of measurement being used in common by all those engaged in making the determinations.

⁴ See Landolt, "The Optical Rotation of Organic Substances," 2nd Ed., pp. 500, 680, 687.

⁵ Skraup, *Monatsh.*, 20, 571, 585 (1899); 22, 171, 253 (1901); Böttcher and Horowitz, *Ibid.*, 32, 793 (1911).

⁶ Biddle and Rosenstein, *THIS JOURNAL*, 35, 418 (1913).

determined by the two methods agreed within the limits of experimental error.

A further comparison was made (Table I) by estimating the amount of conversion of cinchonine into cinchotoxine in a given time under like conditions. In this case the results of the polarimetric method were compared with those of the earlier ether-extraction method already mentioned. In applying this procedure the cinchonine was precipitated, freed as far as possible from cinchotoxine and weighed as the free alkaloid, the cinchotoxine being determined by difference. The results as in the previous case point to the conclusion that under the conditions of the experiments the gravimetric and polarimetric methods are comparable within the limits of experimental error.

TABLE I.—SOLUTIONS CONTAINING ACETIC ACID AND CINCHONINE (0.25 MOLAL) WERE HEATED FOR 15 HOURS AT 99.7° ($\pm 0.2^{\circ}$).

Strength of acid.	Cinchonine recovered from 7.35 g.	Cinchotoxine by difference.	Average per cent. of cinchotoxine.	Per cent. of cinchotoxine from polarimetric reading.
0.75 molal.....	2.4535 2.4070	4.8965 4.9430	66.92	66.50
1.25 molal.....	1.0395 0.9997	6.3105 6.4503	86.82	86.86
1.50 molal.....	0.8320 0.7624	6.5180 6.5876	89.14	88.60
1.75 molal.....	0.5225 0.5666	6.8275 6.7834	92.46	92.60

The measurements presented in this article were made like those recorded in the previous paper by means of a Franz Schmidt and Haensch quartz wedge saccharimeter. The source of light was a Welsbach burner, a bichromate cell being used as a light filter. All readings were taken after the solutions had stood for a time in the dark room. In all cases in which the optical method was used the rotations were determined in terms of the arbitrary scale of the instrument (Ventzke degrees), it being unnecessary for all purposes of calculation to reduce the readings to angular degrees.

In general it may be noted that the initial readings of similar cinchonine solutions vary a trifle in rotation. This may be due to slight variations in the quality of the cinchonine (*e. g.*, minute changes to cinchotoxine) but is probably in part to be ascribed to small experimental errors. Since the same variation would naturally persist throughout any one set of readings, the error introduced into the calculation is negligible. It may be noted, further, that there is a slight increase in optical activity with increasing amount of acid present. On the other hand the rotatory power of cinchotoxine salts appears to vary to a negligible extent with varying concentration of acid. The angular variation observed in this case, however, is somewhat larger than that noted

by Biddle and Rosenstein. They obtained, for a solution of base containing 0.1 molal cinchotoxine and 1.5 molal acetic acid in a dm. tube, a reading of 2.08° , and, for a similar solution containing 3.0 molal acetic acid, a reading of 2.7° .

The cinchotoxine employed in the determinations recorded in Table II was heated with an excess of acetic acid for two days to insure the conversion of any unchanged cinchonine into the alteration product. It was thereupon precipitated as the free base, dissolved in ether and the ethereal solution dried with calcium carbide. After the evaporation of the ether, the base was dried in a vacuum desiccator over sulfuric acid for one week and was finally heated under diminished pressure for two hours at 100° . Readings were made by two observers, (x') and (x''). The objection might be raised that the cinchotoxine thus obtained was not absolutely pure. Since, however, it represents the total alteration product, the optical rotation of which is the value to be determined, the objection may be waived.

TABLE II.

Length of tube—0.25 dm.

Concentration of cinchotoxine—0.1 molal.

Acetic acid, 0.4 molal.		Acetic acid, 1.0 molal.	
(x').	(x'').	(x').	(x'').
0.82	0.766	0.72	0.716
0.82	0.816	0.72	0.696
0.70	0.716	0.82	0.696
0.67	0.766	0.72	0.746
0.82	0.736	0.72	0.816
			0.716
Mean, 0.766		0.74	0.731

From Table II it will be noted that the difference between the readings for 0.4 equivalent of acid and 1.0 equivalent is not greater than the experimental error involved. The average of all the readings is 0.75° , or for a 1 dm. tube as used by Biddle and Rosenstein, 3.00° —a little higher than their higher value. If we ignore the objection which may be raised to the employment of the shorter tube, the angular rotation of cinchotoxine in the presence of acetic acid of concentration varying from 0.4 molal to 1.0 molal, may be regarded as practically constant.

3. Experimental Details.—In determining the rate of conversion of cinchonine into cinchotoxine in various acid solutions, the reaction mixture was kept at a constant temperature (in the greater number of cases at 99.7° (± 0.2)), during the course of the experiment. In some instances the reaction was carried on in small flasks, fitted with a siphon and a reflux condenser. In most cases the reaction mixture was enclosed in a series of hermetically sealed tubes. This method of procedure not only simplified the operation, but also precluded any chance of error due to loss through evaporation or of inaccuracy due to insufficient stirring when

the sample was taken. In the first case, at different time intervals, after quickly stirring the mixture by blowing air back through the siphon, 10 cc. samples were drawn off, rapidly chilled and placed in a dark room until the reading was taken; in the second, at each time interval, a tube was removed and treated as the sample in the previous case. The results obtained by the two methods for solutions of equal concentration were practically identical.

The heating was carried out in a copper water bath about 2 feet square and 8 inches high, fitted with a constant level and heated by means of a quadruple burner. When placed in a small hood to shield the apparatus from currents of air, it was found that the rapidly boiling bath could be readily maintained at a temperature presenting variations in any one set of experiments not exceeding $\pm 0.2^\circ$. In a thermostat of this size it became possible to run a number of determinations practically simultaneously.

As previously indicated,¹ if the reaction is a monomolecular one with respect to the alkaloid, then the rate of the reaction for any particular strength of the catalyzer is expressed by the equation,

$$-d(c)/dt = K(c),$$

where c is the concentration of the alkaloid at the time t , and K is the specific reaction rate. On integration this gives for the value of the specific reaction rate,

$$K_1 = 1/t \log c_0/c_1, \quad (1)$$

where K_1 is the specific reaction rate, t is the time, c_0 is the concentration of the alkaloid at the beginning of the experiment, and c_1 its concentration after the time t . Or, if the calculation is made during different time intervals,

$$K_2 = \frac{1}{t_2 - t_1} \log \frac{c_1}{c_2}, \quad (2)$$

where c_1 is the concentration after the time t_1 , and c_2 the concentration after the time t_2 .

If concentrations are replaced by polarimetric readings, Formula 1 becomes,

$$K_1 = \frac{1}{t} \log \frac{a_0 - a_\infty}{a_1 - a_\infty}, \quad (3)$$

and Formula 2 becomes,

$$K_2 = \frac{1}{t_2 - t_1} \log \frac{a_1 - a_\infty}{a_2 - a_\infty}. \quad (4)$$

In these formulas, a_0 is the instrument reading for the unchanged cinchonine solution, a_1 and a_2 the readings for the solution after the time intervals t_1 and t_2 , and a_∞ the reading for the solution when the cinchonine is completely converted into cinchotoxine.

¹ Biddle and Rosenstein, *THIS JOURNAL*, 35, 421 (1913).

4. **Rate of the Reaction with Acetic Acid.**—In the previous measurements of Biddle and Rosenstein¹ the concentrations of the acid were tabulated as molal concentrations above the acid necessary to form the diacid salt of cinchonine. In recording the present experiments, it has seemed preferable to give the molal concentration of the *total* acid, present including as well that which is naturally in combination with the cinchonine to form a salt. In the following tables, *Cin.* represents the molal concentration of the cinchonine, *L* the length of the polarimeter tube, *T* the temperature of the thermostat, *t* the time in hours and *a* the polarimetric reading of the solution after being heated for time *t*. The polarimetric reading of the solution in which complete conversion to cinchotoxine has been effected is determined from the data given in Table II, it being assumed that the variations in readings due to varying concentration of acid are negligible. These values are given under ∞ .

Under Tables III to XIV are given the actual measurements made in the case of 0.1 molal cinchonine with concentrations of acetic acid ranging from 0.15 to 17.24 molal. Under Tables XV and XVI are recorded simply the resulting rates (K_1 and K_2) obtained for 0.25 molal and 0.01 molal cinchonine, respectively, with varying concentrations of acetic acid.

TABLE III.

Acetic acid, 0.15 molal.

Cin. = 0.1 molal. *L* = 2.0 dm.*T* = 99.7° ($\pm 0.2^\circ$).

<i>t</i>	<i>a</i>	K_1	K_2
0 hr.	34.70
4 hrs.	33.25	0.00563	0.00563
6 hrs.	32.50	0.00577	0.00606
8 hrs.	31.80	0.00578	0.00581
10 hrs.	31.20	0.00564	0.00511
∞ hrs.	6.00	Mean, 0.00570	0.00565

TABLE V.

Acetic acid, 0.2 molal.

Cin. = 0.1 molal. *L* = 1.0 dm.*T* = 99.7° ($\pm 0.1^\circ$).

<i>t</i>	<i>a</i>	K_1	K_2
0 hr.	17.81
5 hrs.	16.40	0.0087	0.0087
7 hrs.	15.75	0.0093	0.0108
9 hrs.	15.26	0.0091	0.0085
11 hrs.	14.73	0.0092	0.0096
16 hrs.	13.54	0.0093	0.0093
∞ hrs.	3.00	Mean, 0.0091	0.0094

TABLE IV.

Acetic acid, 0.175 molal.

Cin. = 0.1 molal. *L* = 1.0 dm.*T* = 99.7° ($\pm 0.2^\circ$).

<i>t</i>	<i>a</i>	K_1	K_2
0 hr.	18.03
4 hrs.	17.10	0.00713	0.00694
8 hrs.	16.18	0.00713	0.00732
12 hrs.	15.35	0.00711	0.00706
16 hrs.	14.56	0.00713	0.00717
∞ hrs.	3.00	Mean, 0.00708	0.00712

TABLE VI.

Acetic acid, 0.4 molal.

Cin. = 0.1 molal. *L* = 0.5 dm.*T* = 99.7° ($\pm 0.2^\circ$).

<i>t</i>	<i>a</i>	K_1	K_2
0 hr.	9.39
2 hrs.	8.55	0.0244	0.0244
4 hrs.	7.92	0.0224	0.0203
6 hrs.	7.17	0.0239	0.0269
8 hrs.	6.55	0.0242	0.0252
11 hrs.	5.81	0.0238	0.0229
∞ hrs.	1.50	Mean, 0.0238	0.0239

* All temperatures reached in this and other papers, it is scarcely necessary to mention, are in the centigrade scale.

¹ THIS JOURNAL, 35, 418 (1913).

TABLE VII.

Acetic acid, 0.8 molal.

Cin. = 0.1 molal. L = 1.0 dm.

T = 99.7° ($\pm 0.2^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	19.80
2 hrs.	16.68	0.0446	0.0446
4 hrs.	14.20	0.0440	0.0434
6 hrs.	12.05	0.0448	0.0463
8 hrs.	10.36	0.0448	0.0449
∞ hrs.	3.00	Mean, 0.0445	0.0448

TABLE VIII.

Acetic acid, 1.0 molal.

Cin. = 0.1 molal. L = 1.0 dm.

T = 99.7° ($\pm 0.1^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	20.32
2 hrs.	16.41	0.0557	0.0557
3 hrs.	14.90	0.0544	0.0520
4 hrs.	13.46	0.0548	0.0560
5 $\frac{1}{4}$ hrs.	11.90	0.0551	0.0561
8 $\frac{3}{4}$ hrs.	8.34	0.0584	0.0634
∞ hrs.	3.00	Mean, 0.0557	0.0566

TABLE IX.

Acetic acid, 1.7 molal.

Cin. = 0.1 molal. L = 1.0 dm.

T = 99.7° ($\pm 0.2^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	20.35
2 $\frac{1}{4}$ hrs.	13.57	0.0782	0.0782
3 $\frac{1}{4}$ hrs.	11.93	0.0768	0.0732
7 hrs.	8.05	0.0767	0.0762
8 hrs.	6.87	0.0817	0.0867
10 hrs.	5.65	0.0816	0.0838
∞ hrs.	3.00	Mean, 0.0790	0.0796

TABLE X.

Acetic acid, 2.0 molal.

Cin. = 0.1 molal. L = 0.5 dm.

T = 99.7° ($\pm 0.2^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	10.19
1 hr.	8.70	0.0817	0.0817
2 hrs.	7.40	0.0841	0.0865
3 hrs.	6.14	0.0908	0.1043
5 $\frac{1}{2}$ hrs.	4.22	0.0917	0.0928
6 $\frac{1}{2}$ hrs.	3.91	0.0916	0.0901
∞ hrs.	1.50	Mean, 0.0880	0.0901

TABLE XI.

Acetic acid, 3.2 molal.

Cin. = 0.1 molal. L = 1.0 dm.

T = 99.7° ($\pm 0.2^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	20.99
2 hrs.	13.68	0.1132	0.1132
4 hrs.	8.66	0.1255	0.1378
6 hrs.	5.76	0.1357	0.1559
8 hrs.	4.61	0.1310	0.1171
10 hrs.	3.80	0.1352	0.1518
∞ hrs.	3.00	Mean, 0.1281	0.1351

TABLE XII.

Acetic acid, 4.0 molal.

Cin. = 0.1 molal. L = 0.5 dm.

T = 99.7° ($\pm 0.2^\circ$).

t.	a.	K ₁ .	K ₂ .
0 hr.	10.50
1 hr.	8.04	0.1387	0.1387
2 hrs.	6.16	0.1429	0.1472
3 hrs.	4.68	0.1506	0.1659
5 $\frac{1}{4}$ hrs.	2.99	0.1487	0.1463
6 hrs.	2.66	0.1483	0.1450
∞ hrs.	1.50	Mean, 0.1458	0.1486

The specific reaction rates as given in the preceding tables (IX and XI) are in agreement with the corresponding values obtained by Biddle and Rosenstein through a slightly different method of heating. If the mean

TABLE XIII.

Acetic acid, 8.0 molal.

Cin. = 0.1 molal. $L = 1.0$ dm. $T = 99.7^\circ (\pm 0.2^\circ)$.

t	a	K_1	K_2
0 hr.	20.31
1 hr.	13.29	0.2259	0.2388
2 hrs.	9.15	0.2247	0.2135
3 hrs.	6.71	0.2230	0.2195
4 hrs.	4.97	0.2359 ¹	0.2749 ¹
5 hrs.	3.92	0.2549 ¹	0.3307 ¹
∞ hrs.	3.00	Mean, 0.2245	0.2229

TABLE XIV.

Acetic acid, 17.24 molal (glacial).²Cin. = 0.1 molal. $L = 0.5$ dm. $T = 99.7^\circ (\pm 0.2^\circ)$.

t	a	K_1	K_2
0 hr.	10.20
1 hr.	7.23	0.1814	0.1814
2 hrs.	5.31	0.1793	0.1772
3 hrs.	4.06	0.1771	0.1727
4 hrs.	3.36	0.1675	0.1387
5 hrs.	2.72	0.1706	0.1832
∞ hrs.	1.50	Mean, 0.1751	0.1706

values of the reaction rate as obtained by them are calculated with t expressed in hours, we obtain the following comparison:

Conc. of acid.	K (Biddle and Rosenstein).	K (Tables IX and XI).
1.7 molal	0.0780 ³	0.0783 ⁴
3.2 molal	0.1296 ³	0.1216 ⁴

In the experiments whose results alone are recorded under Tables XV and XVI, it may be noted that solutions containing the higher concentration of cinchonine (0.25 molal) were sooner discolored by heating, and the readings in most cases were made in a short tube (0.25 dm.). In solutions containing a lower concentration of the alkaloid (0.01 molal), a longer tube (4.0 dm.) was employed. K_1 and K_2 have the same significance as given in the preceding tables.

TABLE XV.

Acetic acid. Cin. = 0.25.

 $T = 99.7^\circ (\pm 0.2^\circ)$.

No.	Normality of total acid.	K_1	K_2
1.....	0.50	0.0200	0.0192
2.....	0.75	0.0310	0.0327
3.....	1.00	0.0414	0.0434
4.....	1.25	0.0563	0.0566
5.....	1.50	0.0721	0.0721
6.....	2.00	0.0880	0.0901
7.....	2.50	0.1072	0.1112

TABLE XVI.

Acetic acid. Cin. = 0.01.

 $T = 99.7^\circ (\pm 0.2^\circ)$.

No.	Normality of total acid.	K_1	K_2
1.....	0.05	0.0056	0.0058
2.....	0.10	0.0086	0.0089
3.....	0.15	0.0116	0.0127
4.....	0.20	0.0153	0.0162
5.....	0.40	0.0252	0.0256
6.....	0.80	0.0340	0.0347

¹ Readings for close of fourth and fifth hours were inexact on account of increased color of solution. Corresponding values of K_1 and K_2 are consequently not considered in determining mean value of these constants.

² 97.85 cc. of glacial acetic containing 0.1 molal cinchonine gave at ordinary temperature a volume of 100 cc.

³ Temperature of experiment, $99.6^\circ (\pm 0.1^\circ)$.

⁴ Temperature of experiment, $99.7^\circ (\pm 0.2^\circ)$.

TABLE XVII.

COMPARATIVE SUMMARY OF DATA DERIVED FROM PRECEDING DETERMINATIONS.

A.				B.				C.			
No.	ac.	K ₂	K ₂ /ac.	No.	ac'.	K ₂	K ₂ /ac'.	No.	ac".	K ₂	K ₂ /ac"
1	0.05	0.0058 ¹	0.116	1	0.04	0.0058 ¹	0.145	1	0.00	0.0094	...
2	0.10	0.0089 ¹	0.089	2	0.05	0.0057	0.104	2	0.00	0.0192 ²	...
3	0.15	0.0127 ¹	0.085	3	0.075	0.0071	0.095	3	0.03	0.0058 ¹	0.193
4	0.15	0.0057	0.038	4	0.09	0.0089 ¹	0.099	4	0.08	0.0089 ¹	0.111
5	0.175	0.0071	0.041	5	0.10	0.0094	0.094	5	0.13	0.0127 ¹	0.098
6	0.20	0.0162 ¹	0.081	6	0.14	0.0127 ¹	0.091	6	0.18	0.0162 ¹	0.090
7	0.20	0.0094	0.047	7	0.19	0.0162 ¹	0.085	7	0.20	0.0239	0.119
8	0.40	0.0239	0.060	8	0.25	0.0192 ²	0.081	8	0.25	0.0327 ²	0.131
9	0.40	0.0256 ¹	0.064	9	0.30	0.0239	0.080	9	0.38	0.0256 ¹	0.067
10	0.50	0.0192 ²	0.041	10	0.39	0.0256 ¹	0.066	10	0.50	0.0434 ²	0.085
11	0.75	0.0327 ²	0.044	11	0.50	0.0327 ²	0.065	11	0.60	0.0448	0.075
12	0.80	0.0448	0.056	12	0.70	0.0448	0.067	12	0.75	0.0566 ²	0.076
13	0.80	0.0347 ¹	0.043	13	0.75	0.0434 ²	0.058	13	0.78	0.0347 ¹	0.045
14	1.00	0.0566	0.057	14	0.79	0.0347 ¹	0.044	14	0.80	0.0566	0.071
15	1.00	0.0434 ²	0.043	15	0.90	0.0566	0.063	15	1.00	0.0721 ²	0.072
16	1.25	0.0566 ²	0.045	16	1.00	0.0566 ²	0.057	16	1.50	0.0796	0.053
17	1.50	0.0721 ²	0.048	17	1.25	0.0721 ²	0.058	17	1.50	0.0901 ²	0.059
18	1.70	0.0796	0.047	18	1.60	0.0796	0.050	18	1.80	0.0901	0.050
19	2.00	0.0901	0.045	19	1.75	0.0901 ²	0.051	19	2.00	0.1112	0.055
20	2.00	0.0901 ²	0.045	20	1.90	0.0901	0.047	20	3.00	0.1351	0.045
21	2.50	0.1112 ²	0.045	21	2.25	0.1112 ²	0.049	21	3.80	0.1486	0.039
22	3.20	0.1351	0.042	22	3.10	0.1351	0.044	22	7.80	0.2229	0.029
23	4.00	0.1486	0.037	23	3.90	0.1486	0.038	23	17.04	0.1706	0.010
24	8.00	0.2229	0.028	24	7.90	0.2229	0.028				
25	17.14	0.1706	0.010	25	17.14	0.1706	0.010				

In the accompanying table (Table XVII) are brought together the various specific reaction rates (K_2) given on the preceding pages, for 0.25, 0.1 and 0.01 molal cinchonine in various concentrations of acetic acid, the latter being tabulated as total acid concentrations under A, as concentrations above the monoacetate under B, and as concentrations above the diacetate under C. Under K_2/ac , K_2/ac' and K_2/ac'' , are given the values obtained by dividing the specific reaction rate, respectively, with the total acid concentration ac , the concentration above the monoacetate ac' , and that above the diacetate ac'' .

In the preceding paper of Biddle and Rosenstein,³ it was suggested that the conversion of cinchonine into cinchotoxine involves at least two elements, of which one is independent of the presence of a weak acid and the other is dependent upon the presence of such an acid. In the study of the catalysis the concentration of the acid was expressed in terms of

¹ Values from solutions 0.01 molal with respect to cinchonine.

² Values from solutions 0.25 molal with respect to cinchonine. Unmarked values from solutions 0.1 molal with respect to cinchonine.

³ THIS JOURNAL, 35, 418 (1913).

the "free" acid, *i. e.*, in terms of the amount in excess of that needed to form the diacetate. A consideration of the summary in Table XVII leads unavoidably to the conclusion that the rate of the reaction is more correctly represented as a function of the acid concentration in excess of that necessary to form the *monoacetate*. This concentration of acid may, consequently, be provisionally designated as "free" acid, although as will be pointed out in a later paper, even this value does not exactly represent the factor in the organic acid responsible for the catalyzing action. Indeed, as will be later shown the rate of the reaction is a linear function of the molecular concentration of the undissociated organic acid in the solution—a value which while in most cases approaching that of the concentration of the acid in excess of the *monoacetate* is not exactly represented by this concentration, nor by that of the acid in excess of the *diacetate*.

Since, however, increasing concentration of acid above the *monoacetate* is accompanied by increasing rate of reaction, it becomes of interest to study the graph presented by plotting these values against each other, as shown in Fig. 1. This is of particular interest in seeking for some ex-

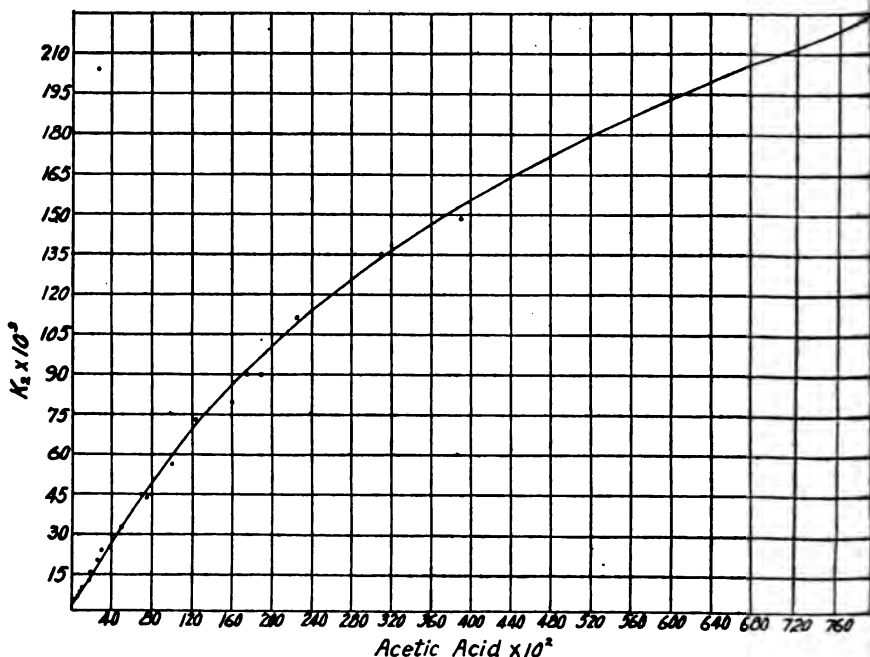


Fig. 1.

planation for the apparent anomaly observed in the specific reaction rates of cinchonine diacetate, where different concentrations of the alkaloid lead to widely divergent values for K_2 (compare values for K_2 under Nos.

1 and 2, C, Table XVII). If the reaction is monomolecular with respect to the cinchonine salt, and the catalyzer obeys the ordinary mass law, the values of K_2 for different concentrations of cinchonine salt should not differ appreciably in like concentrations of the catalyzing acid. If now, in the cases considered, the reaction is regarded as monomolecular with respect to the cinchonine monoacetate and the acid in excess of that necessary to form this salt is regarded as representing the concentration of the catalyzer, the values of K_2 will be found in general to increase with increasing concentration of acid (see B, Table XVII).

It will be observed, furthermore, that the increasing values of K_2 correspond with fair uniformity in the case of all three different concentrations of cinchonine. It may, consequently, be assumed that the first equivalent of acid needed to form the monacid salt does not exert a large catalyzing influence upon the speed of the reaction. This is in accord with an observation already made in a previous paper¹ that the catalyzing influence of acetic acid upon different monacid salts of cinchonine is apparently not greatly different. In stating this, however, attention must be called to the fact that the catalytic action of a given concentration of an organic acid upon different monacid salts of cinchonine does not lead to *identical* reaction rates. This is clearly shown on comparing the action of acetic acid on cinchonine monoacetate and cinchonine monohydrochloride, respectively (see Table XXXIV).

It is of further interest to note the general relation between the speed of the reaction and the concentration of the organic acid. In the fourth column of B, Table XVII, are presented under K_2/ac' , as shown, the quotient of the specific reaction rate divided by the concentration of the acid in excess of that forming the monoacetate. As is seen the value of K_2/ac' gradually decreases with increasing concentration of acid.

5. Rate of the Reaction with Acids other than Acetic.—Biddle² found that under like conditions the amount of cinchonine changed into cinchotoxine was less with strong acids than it was with weak. In the following tables are given the results obtained from a study of this catalysis in the presence of acids of quite different dissociation constants. In Tables XVIII to XXV inclusive, the actual measurements are given in detail. In Table XXVI are summarized the results presented in the preceding tables, together with the resulting rates of other experiments, the details of which, to conserve space, have been omitted. Chloroacetic acid is inadmissible in this study on account of its ready hydrolysis under the conditions of the experiment into hydrochloric and oxyacetic acids. This will account for the low catalyzing influence of this acid already observed,³

¹ Biddle, *Ber.*, 45, 2836 (1912).

² *THIS JOURNAL*, 34, 500 (1912).

³ Biddle, *Ibid.*, 34, 501 (1912).

TABLE XVIII.

Formic acid, 0.2 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	20.20
6 hrs.	19.03	0.0051	0.0051
10 hrs.	18.23	0.0053	0.0056
12 hrs.	17.73	0.0056	0.0072
16 hrs.	16.81	0.0060	0.0070
28 hrs.	14.70	0.0060	0.0060
∞ hrs.	3.00 ¹	Mean, 0.0056	0.0062

TABLE XX.

Propionic acid, 0.2 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	17.77
2 hrs.	17.10	0.0101	0.0101
4 hrs.	16.41	0.0105	0.0109
5 $\frac{1}{2}$ hrs.	15.81	0.0112	0.0133
8 $\frac{1}{4}$ hrs.	14.94	0.0111	0.0111
11 $\frac{1}{4}$ hrs.	13.91	0.0117	0.0130
∞ hrs.	3.00	Mean, 0.0109	0.0117

TABLE XXII.

Oxalic acid, 0.2 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	20.88
4 hrs.	20.14	0.0046	0.0046
8 hrs.	19.54	0.0042	0.0039
12 hrs.	19.00	0.0040	0.0036
16 hrs.	18.43	0.0040	0.0039
24 hrs.	17.33	0.0040	0.0040
∞ hrs.	3.00	Mean, 0.0042	0.0040

TABLE XIX.

Formic acid, 0.8 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	21.73
4 hrs.	19.35	0.0148	0.0148
8 hrs.	17.29	0.0147	0.0147
12 hrs.	15.13	0.0157	0.0157
16 hrs.	13.33	0.0161	0.0157
24 hrs.	10.41	0.0168	0.0157
∞ hrs.	3.0	Mean, 0.0156	0.0156

TABLE XXI.

Propionic acid, 0.8 molal.
Cin. = 0.1 molal. $L = 0.5$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	9.87
2 hrs.	7.91	0.0579	0.0579
4 hrs.	6.42	0.0577	0.0577
5 $\frac{1}{2}$ hrs.	5.40	0.0603	0.0603
7 hrs.	4.70	0.0597	0.0597
11 $\frac{1}{4}$ hrs.	3.18	0.0620	0.0620
∞ hrs.	1.50	Mean, 0.0595	0.0603

TABLE XXIII.

Oxalic acid, 0.3 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t.</i>	<i>a.</i>	K_1	K_2
0 hr.	21.02
8 hrs.	20.70	0.0010	0.0010
12 hrs.	20.22	0.0016	0.0016
16 hrs.	19.87	0.0018	0.0018
24 hrs.	19.20	0.0019	0.0019
30 hrs.	18.96	0.0017	0.0017
∞ hrs.	3.00	Mean, 0.0016	0.0016

In the presence of 0.25 *N* hydrochloric acid the rate but slightly exceeds 0.0001, the conversion after several hours being so slight as to render the experimental results more or less inexact. With concentrations of 0.4 m and above with respect to the acid, there was no decrease in rotation on heating. Indeed, with these concentrations, an apparent slight increase

¹ This is the reading for the corresponding cinchotoxine solution in acetic acid it being assumed that the variation due to the presence of different acids is sufficiently small to be negligible.

TABLE XXIV.

Hydrochloric acid, 0.15 molal.
Cin. = 0.1 molal. $L = 4.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t</i>	α	K_1	K_2
0 hr.	78.42
2 $\frac{3}{4}$ hrs.	77.83	0.00141	0.00141
4 $\frac{1}{4}$ hrs.	77.44	0.00136	0.00129
7 hrs.	76.70	0.00163	0.00219

∞ hrs. 12.00 Mean, 0.00147 0.00163

TABLE XXV.

Hydrochloric acid, 0.175 molal.
Cin. = 0.1 molal. $L = 4.0$ dm.
 $T = 99.7^\circ (\pm 0.2^\circ)$.

<i>t</i>	α	K_1	K_2
0 hr.	84.01
6 hrs.	83.41	0.00061	0.00061
8 hrs.	83.09	0.00070	0.00097
12 hrs.	82.60	0.00072	0.00075

∞ hrs. 12.00 Mean, 0.00068 0.00077

in rotation is generally observed, which, however, gradually falls to the original reading. Thus, with 0.8 molal hydrochloric acid the following readings were obtained:

Time:	0 hr.	4 hrs.	8 $\frac{1}{4}$ hrs.	12 hrs.	15 $\frac{3}{4}$ hrs.	23 $\frac{3}{4}$ hrs.	28 hrs.
	20.96	21.30	21.30	21.46	21.09	21.03	20.85

The cause of this phenomenon was not determined. It scarcely seems due to mutarotation, nor is it probably to be ascribed to the formation of isomers of cinchonine such as isocinchonine prepared by Hesse.¹

TABLE XXVI.

Nor- mality of total acid.	Propionic acid.		Acetic acid.		Formic acid.		Oxalic acid.		Hydrochloric acid.	
	K_1	K_2	K_1	K_2	K_1	K_2	K_1	K_2	K_1	K_2
1 0.15	0.00570	0.00565	0.00147	0.00163
2 0.175	0.00708	0.00712	0.00068	0.00077
3 0.20	0.0109	0.0117	0.0091	0.0094	0.0056	0.0062	0.0003 ²	0.0003 ²
4 0.25	0.0001 ²	0.0001 ²
5 0.40	0.0278	0.0296	0.0238	0.0239	0.0118	0.0121	0.0042	0.0040
6 0.60	0.0016	0.0019
7 0.80	0.0595	0.0611	0.0488	0.0499	0.0156	0.0165
8 1.00	0.0567	0.0574
9 1.20	0.0750	0.0760
10 1.70	0.0790	0.0796
11 2.00	0.0880	0.0901	0.0007 ²	0.0007 ²
12 3.20	0.1275	0.1351

In Table XXVI is presented a comparative summary of the results obtained with different acids. In the results here tabulated it is interesting to note that the speed of the conversion in every instance decreases with acids of increasing dissociation constant—a fact to which attention has already been called in an earlier article.³ In the presence of any one of the three acids, propionic, acetic, or formic, increasing concentration of acid leads to increasing speed of conversion; in the presence of oxalic acid or hydrochloric acid, the reverse is true. In the case of the first three

¹ *Ann.*, 276, 91 (1893).

² Approximate value only.

³ Biddle, *This Journal*, 34, 500 (1912).

acids the rate of increase of speed with equal increments in concentration of acid is greatest with the acid of lowest dissociation constant, and least with the acid of highest dissociation constant. If now this is due primarily to the increasing concentration of H^+ ion in the case of the more highly dissociated acids, it would be natural to expect that, in studying acids of increasing dissociation constant the effect of the increasing concentration of H^+ ion with increasing concentration of acid would eventually exceed that of the positive catalytic influence of the organic acid. In this case, as with oxalic acid, the speed would diminish with increasing concentration of acid. In the case of an acid such as oxalic it would be of interest to study the effect of still lower concentrations to determine whether the speed passes through a maximum value, below which increasing concentration of acid would exhibit the same positive catalyzing action shown in the case of organic acids less dissociated.

In the case of hydrochloric acid, if we assume that this acid has no positive catalytic influence similar to that of an organic acid, then the decreasing speed of the reaction with increasing concentration of acid becomes a measure of the influence of the H^+ ion—a matter which will be considered in detail in a later paper.

6. Rate of the Reaction with Mixtures of Hydrochloric Acid and Acetic Acid.—The inhibiting influence of increasing concentration of H^+ , as previously noted,¹ ion upon the catalysis renders the determination of the reaction velocity in solutions containing mixtures of the two acids, hydrochloric and acetic, of particular interest. Since dilute hydrochloric acid may be regarded practically as completely dissociated, we may, to a certain extent, vary as desired the concentration of H^+ ion by choosing a suitable mixture of the two acids. Furthermore, since solutions of cinchonine in dilute hydrochloric acid exhibit no large velocity of conversion, as is shown in solutions of like H^+ ion concentration containing acetic acid,² it seems safe, as already indicated, to disregard any *positive* catalyzing influence of the halogen acid. It then becomes possible through a study of mixtures of the two acids to gain some idea of the retarding influence of the H^+ ion upon the positively accelerating action of the acetic acid. The experimental results of such a study are presented in the following determinations in which are first considered the reaction rates in the case of cinchonine in molal acetic acid with varying amounts of hydrochloric acid.

In Table XXXIII is presented a summary of the results obtained in the following measurements (Tables XXVII–XXXII) together with the results of similar experiments, the detailed measurements of which have been omitted.

¹ Biddle, *THIS JOURNAL*, 34, 505 (1912).

² *Ibid.*, *Loc. cit.*

TABLE XXVII.

Hydrochloric acid, 0.1 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	20.73
1 hr.	16.73	0.0370	0.0370
2 hrs.	14.31	0.0391	0.0421
3 hrs.	13.24	0.0397	0.0432
4 hrs.	11.39	0.0382	0.0346
5 hrs.	10.36	0.0382	0.0379
6 hrs.	3.00	Mean, 0.0384	0.0389

TABLE XXIX.

Hydrochloric acid, 0.15 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	21.30
1 hr.	19.47	0.0229	0.0229
2 hrs.	17.90	0.0223	0.0217
3 hrs.	16.36	0.0228	0.0237
4 hrs.	14.71	0.0228	0.0229
5 hrs.	13.58	0.0226	0.0220
6 hrs.	3.00	Mean, 0.0227	0.0227

TABLE XXXI.

Hydrochloric acid, 0.2 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	21.72
1 hr.	21.31	0.0048	0.0048
2 hrs.	20.95	0.0046	0.0043
3 hrs.	20.51	0.0048	0.0054
4 hrs.	20.06	0.0048	0.0046
5 hrs.	19.40	0.0041	0.0031
6 hrs.	3.00	Mean, 0.0046	0.0044

TABLE XXVIII.

Hydrochloric acid, 0.125 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	21.13
1 hr.	18.61	0.0325	0.0325
2 hrs.	16.92	0.0287	0.0249
3 hrs.	15.79	0.0303	0.0367
4 hrs.	14.80	0.0311	0.0349
5 hrs.	12.83	0.0313	0.0317
6 hrs.	3.00	Mean, 0.0308	0.0321

TABLE XXX.

Hydrochloric acid, 0.175 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	21.62
1 hr.	20.48	0.0122	0.0122
2 hrs.	19.47	0.0133	0.0148
3 hrs.	18.38	0.0138	0.0149
4 hrs.	17.77	0.0138	0.0141
5 hrs.	16.39	0.0139	0.0142
6 hrs.	3.00	Mean, 0.0136	0.0140

TABLE XXXII.

Hydrochloric acid, 0.21 molal.
Acetic acid, 1.0 molal.
Cin. = 0.1 molal. $L = 1.0$ dm.
 $T = 99.7^\circ (\pm 0.1^\circ)$.

t.	a.	K ₁	K ₂
0 hr.	21.41
1 hr.	21.10	0.0018	0.0018
2 hrs.	20.81	0.0019	0.0020
3 hrs.	20.52	0.0021	0.0024
4 hrs.	20.19	0.0021	0.0021
5 hrs.	3.00	Mean, 0.0020	0.0021

In Table XXXIV is given a comparative summary of the specific reaction rates of cinchonine monoacetate, cinchonine monohydrochloride and cinchonine dihydrochloride in the presence of varying quantities of acetic acid. To conserve space the detailed measurements in the case of the two hydrochlorides have been omitted and the results alone recorded.

TABLE XXXIII.

No.	Molality of cinchonine.	Normality of acetic acid.	Normality of hydrochloric acid.	K_1 .	K_2 .
1.....	0.1	1.0	...	0.0557	0.0566
2.....	0.1	1.0	0.100	0.0384	0.0389
3.....	0.1	1.0	0.125	0.0308	0.0321
4.....	0.1	1.0	0.150	0.0227	0.0227
5.....	0.1	1.0	0.175	0.0136	0.0140
6.....	0.1	1.0	0.200	0.0046	0.0044
7.....	0.1	1.0	0.210	0.0020	0.0021
8.....	0.1	1.0	0.220	0.0013	0.0015
9.....	0.1	1.0	0.230	0.0009	0.0011
10.....	0.1	0.5	0.15	0.0131	0.0136
11.....	0.1	0.5	0.25	0.0003	0.0005
12.....	0.01	0.5	0.010	0.0158	0.0163
13.....	0.01	0.5	0.015	0.0115	0.0114
14.....	0.01	0.5	0.020	0.0054	0.0056

TABLE XXXIV.

No.	Molality of cinchonine.	Normality of acetic acid.	Normality of hydrochloric acid.	K_1 .	K_2 .
1.....	0.1	0.2	0.0091	0.0094
2.....	0.1	0.4	0.0238	0.0239
3.....	0.1	0.8	0.0445	0.0448
4.....	0.1	1.0	0.0557	0.0566
5.....	0.1	1.7	0.0790	0.0796
6.....	0.09	0.1	0.09	0.0069	0.0076
7.....	0.09	0.2	0.09	0.0125	0.0115
8.....	0.09	0.4	0.09	0.0215	0.0216
9.....	0.09	0.8	0.09	0.0325	0.0339
10.....	0.09	1.6	0.09	0.0545	0.0548
11.....	0.1	0.1	0.20	0.00066	0.0006
12.....	0.1	0.2	0.20	0.0011	0.0010
13.....	0.1	0.4	0.20	0.0018	0.0017
14.....	0.1	0.8	0.20	0.0029	0.0030
15.....	0.1	2.0	0.20	0.0065	0.0068
16.....	0.1	0.2	0.30	0.0000	0.0000
17.....	0.1	2.0	0.30	0.0000	0.0000

A consideration of Tables XXXIII and XXXIV clearly reveals the effect of varying concentrations of hydrochloric acid under widely divergent conditions. With increasing concentration of the halogen acid, the acetic acid remaining constantly normal, the speed of the reaction falls from a maximum value of $K_2 = 0.0566$ in the presence of normal acetic acid alone to $K_2 = 0.00$ when the concentration of hydrochloric acid has reached a value of 0.3 *N*. While the hydrochloric acid, even if it were completely dissociated, cannot on account of its partial use to neutralize the cinchonine be regarded as exactly representing the concentration of H^+ ion, yet the general inhibiting effect of increasing concentration of this ion in solutions

of constant concentration with respect to the organic acid is clearly seen from the data presented.

The inhibiting action of the H^+ ion appears no less clearly in the results obtained with constant concentration of halogen acid and varying amounts of acetic acid (Table XXXIV). As will be seen, increasing concentration of organic acid effects increasing speed of reaction in the case of cinchonine acetate, cinchonine monohydrochloride and cinchonine dihydrochloride, and for any given concentration of organic acid, the speed is greatest in the first instance, less in the second and least in the third.

It is of further interest to observe that the ratio between speeds in the case of different salts with equal concentrations of organic acid appears to approach a constant, as is shown in a comparison of the monohydrochloride with the dihydrochloride in Table XXXV.

TABLE XXXV.

No.	Normality of acetic acid.	Ratio of speed, monohydrochloride: dihydrochloride.
1.....	0.1	$\frac{0.0076}{0.00066} = 11.5$
2.....	0.2	$\frac{0.0115}{0.0010} = 11.5$
3.....	0.4	$\frac{0.0216}{0.0017} = 12.7$
4.....	0.8	$\frac{0.0339}{0.0030} = 11.3$

From these considerations and others which have been presented in this paper, it will be evident that a definite interpretation of this catalysis involves a fairly exact determination on the one hand of the concentration of the H^+ ion in the solution and on the other of the concentration of the nonionized organic acid. The methods employed in such determination, and the results obtained, will be presented in a later paper by the senior author of the present article. In this it will be shown that the conversion of cinchonine into cinchotoxine is fundamentally dependent upon the presence of the univalent cinchonine ion and that the speed of the reaction is a function of the concentration of the undissociated organic acid.

Summary.

1. The rate of conversion of cinchonine into cinchotoxine gradually increases with increasing concentration of an organic acid such as acetic acid, the range of concentration of acid through which this was studied and found to be true extending from 0.05 molal to and beyond 8.0 molal. Within this range the speed of the reaction appears to be some direct function of the concentration of the nonionized organic acid. In glacial acetic acid (17.24 molal), the rate decreases somewhat, falling considerably below that shown in 8.0 molal acid.

2. The speed of the reaction in the presence of different organic acids of equal concentration diminishes with increasing values of the dissociation constants of the respective acids.

3. The function of the organic acid is that of a true catalytic agent, accelerating but not causing the reaction, as is shown by the fact that cinchonine dihydrochloride gives a low but measurable rate of conversion.

4. The effect of H^+ ion is to inhibit the rate of the reaction. In solutions of uniform concentration with respect to cinchonine (0.1 molal) and acetic acid (1.0 molal), increasing concentration of H^+ ion, as effected by the introduction of hydrochloric acid, produces a decrease in the rate of conversion until the reaction practically ceases when the solution contains 0.3 molal hydrochloric acid. In solutions of different salts of the alkaloid, such as cinchonine acetate, cinchonine monohydrochloride and cinchonine dihydrochloride, increasing concentration of organic acid effects increasing rate of reaction. The rates for equal concentration of organic acid, however, are less in the case of the salts naturally presenting through partial hydrolysis in solution the greater concentration of H^+ ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

THE RATE OF CONVERSION OF CINCHONIDINE INTO CINCHOTOXINE.¹

(ON CATALYSIS WITH WEAK ACIDS, VII.)

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Received July 19, 1915.

1. Introduction.—Cinchonidine was isolated from the bark of the cinchona trees by Winkler in 1847.² The alkaloid crystallizes from alcohol in white prisms which melt at 202–203°. It is isomeric in composition with cinchonine, but unlike this base is strongly laevorotatory. As shown by Königs and Hussmann,³ it is possible to convert one alkaloid directly into the other. Thus, on prolonged heating with amyl alcohol and potassium hydroxide, cinchonine is converted into cinchonidine.

The properties of the two alkaloids indicate that they are of like constitution, the relation between the two being one of stereoisomerism. As was early shown by Pasteur,⁴ both may be converted into the common product, cinchotoxine.

¹ See preceding article on "Rate of Conversion of Cinchonine into Cinchotoxine."

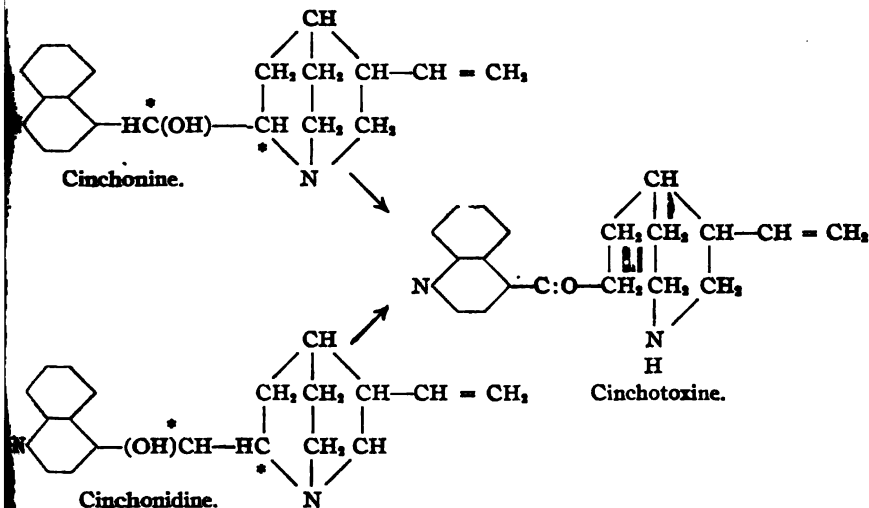
² *Rep. f. Pharm.*, 85, 392; 98, 384; 99, 1.

³ *Ber.*, 29, 2185 (1896).

⁴ *Jahresb.*, 1853, 422; *Compt. rend.*, 37, 110 (1853); *Ann.*, 88, 209 (1853).

If, in the light of the numerous investigations¹ of Königs, v. Miller, Rabe, Rhode and Skraup, the constitutions of cinchonine, cinchonidine and cinchotoxine are represented as in Fig. 1, the conversion of the first two alkaloids into the third involves the loss of asymmetry of the two asymmetric carbon atoms starred. The difference between cinchonine and cinchonidine must, consequently, lie in the stereoisomeric arrangement about one or both of these two carbon atoms.

According to Rabe² the difference between the two alkaloids is determined solely by the difference in stereoisomeric arrangement about the asymmetric carbon atom within the ring.



An investigation of the conversion of cinchonidine into cinchotoxine in comparison with the similar conversion of cinchonine into this base under like conditions thus becomes of interest as casting light upon the influence of stereoisomerism upon this conversion.

2. The Conversion of Cinchonidine into Cinchotoxine in the Presence of Organic Acids.—In view of the peculiar catalytic action of organic acids upon the rate of conversion of cinchonine into cinchotoxine, it is of importance to determine first whether the same phenomena obtain in the case of the stereoisomeric cinchonidine. That a like catalyzing influence occurs in this case as well has been indicated in a previous paper³ and has also been pointed out by Rabe.⁴ To obtain a general comparison

¹ *Ann.*, 347, 143 (1906); 350, 180 (1906); 364, 330 (1909); 365, 353 (1909); 373, 85 (1910).

² *Ann.*, 373, 91 (1910).

³ Biddle and Rosenstein, *THIS JOURNAL*, 35, 419 (1913).

⁴ *Ber.*, 45, 2929 (1912).

of the influence of different acids upon this catalysis, the following experiments were made with hydrochloric, formic and acetic acids: To 2 g. of cinchonidine were added in each case 5 equivalents of acid and then sufficient water to give a solution of 40 cc. The various solutions with the different acids were then heated at $99.7^\circ (\pm 0.2^\circ)$ for 24 hours. Thereupon the alkaloids were precipitated by the addition of sodium hydroxide, extracted with ether and the solutions dried with calcium carbide. The ethereal solution of cinchotoxine was in each case thus largely freed from cinchonidine which, like cinchonine, is difficultly soluble in dry ether. The weight of the cinchotoxine was obtained on evaporating the ether. The results in each case were checked by isolating and weighing the unchanged cinchonidine. The results obtained are given in Table I.

TABLE I.
Cinchonidine, 2.0 grams. Temp., $99.7^\circ (\pm 0.2^\circ)$.

No.	Acid.	Dissociation constant at 18° .	Cinchotoxine formed. Grams.	Per cent. conversion.
1.....	Hydrochloric	0.05	0.25
2.....	Formic	0.0214	1.15	60.00
3.....	Acetic	0.0018	1.92	96.00

While the results of these experiments are to be regarded as only rough approximations, they show beyond doubt the same catalyzing action observed in the case of cinchonine under like conditions.

For the exact measurement of the speed of the reaction advantage was taken, as in the case of cinchonine, of the variation in the optical rotation of the solution as the conversion progressed. As has been shown in previous papers, the value of the specific reaction rate is,

$$K_1 = \frac{1}{t} \log \frac{a_0 - a_\infty}{a_1 - a_\infty} \quad (1)$$

or, if instead of calculating K from the time when the reaction began, the calculation is made during different time intervals,

$$K_2 = \frac{1}{t_2 - t_1} \log \frac{a_1 - a_\infty}{a_2 - a_\infty} \quad (2)$$

In these equations, as previously given, a_0 is the reading of the saccharimeter for the cinchonine solution, a_1 and a_2 the readings for the solution after the time intervals t_1 and t_2 , and a_∞ the reading for the corresponding cinchotoxine solution. In the results recorded in this paper the calculations were made as in the case of cinchonine, bearing in mind, of course, that the specific rotation of cinchonidine unlike that of cinchonine is negative.

3. The Rate of Conversion in the Presence of Acetic Acid and Formic Acid.—In Tables II and III are given in detail the measurements for two concentrations of acetic acid. In Table IV are recorded the values of K_1 and K_2 for all the experiments carried out with acetic acid alone and formic acid alone. In this table and the remaining tables of the paper, to

conserve space, there are given only the resulting values of K_1 and K_2 for the various experiments made.

TABLE II.

Acetic acid, 0.2 molal.

Cin. = 0.1 molal. $L = 1.0$ dm. $T = 99.7^\circ (\pm 0.2^\circ)$.

t.	a.	K_1	K_2
0 hr.	-11.05
4 hrs.	-10.25	0.0064	0.0064
6 hrs.	-9.75	0.0070	0.0084
8 hrs.	-9.30	0.0072	0.0078
12 hrs.	-8.35	0.0077	0.0087
∞ hrs.	3.00	Mean, 0.0071	0.0078

TABLE III.

Acetic acid, 0.3 molal.

Cin. = 0.1 molal. $L = 1.0$ dm. $T = 99.7^\circ (\pm 0.2^\circ)$.

t.	a.	K_1	K_2
0 hr.	-11.40
4 hrs.	-9.80	0.0128	0.0128
6 hrs.	-9.20	0.0120	0.0104
8 hrs.	-8.50	0.0122	0.0128
12 hrs.	-7.10	0.0128	0.0141
∞ hrs.	3.00	Mean, 0.0125	0.0125

TABLE IV.

Cin. = 0.1 molal. $T = 99.7^\circ (\pm 0.2^\circ)$.

No.	Normality of total acid.	Acetic acid.		Formic acid.		Oxalic acid.	
		K_1	K_2	K_1	K_2	K_1	K_2
1	0.2	0.0071	0.0078	0.0048	0.0050
2	0.3	0.0125	0.0125	0.0077	0.0076
3	0.4	0.0178	0.0180	0.0102	0.0095
4	0.5	0.0241	0.0238	0.0118	0.0113	0.0033	0.0031
5	0.8	0.0373	0.0370
6	1.5	0.0585	0.0586
7	3.0	0.1040	0.1053

A comparison of the results in Table IV with those obtained under like conditions in the case of cinchonine (see THIS JOURNAL, p. 2077), show that we are dealing with a similar type of catalysis in the two cases. In both instances in the presence of acetic acid and formic acid there is increasing rate of reaction with increasing concentration of acid.

4. The Rate of Conversion with Mixtures of Acetic and Hydrochloric Acids.—In Table V are given the rates of the reaction in the case of cinchonidine monohydrochloride and cinchonidine dihydrochloride in the presence of varying quantities of acetic acid.

TABLE V.

No.	Molality of cinchonidine.	Normality of acetic acid.	Normality of hydrochloric acid.	K_1	K_2
1.....	0.09	0.2	0.09	0.0097	0.0098
2.....	0.09	0.3	0.09	0.0136	0.0138
3.....	0.09	0.4	0.09	0.0165	0.0170
4.....	0.09	0.8	0.09	0.0272	0.0275
5.....	0.09	1.5	0.09	0.0402	0.0418
6.....	0.1	0.2	0.2	0.0009	0.00084
7.....	0.1	0.3	0.2	0.0010	0.0012
8.....	0.1	0.5	0.2	0.0016	0.0018
9.....	0.1	0.8	0.2	0.0025	0.0027
10.....	0.1	1.5	0.2	0.0040	0.0044

A comparison of the specific reaction rates from Table V with those from the corresponding tables under the study of cinchonine (see preceding article), clearly reveals the close resemblance between the results in the two cases. In both instances the catalyzing influence of the organic acid accelerates the rate of reaction, and in both instances this accelerating influence is greatest in the case of the monoacetate, less in the case of the monohydrochloride and least in the case of the dihydrochloride.

It is of further interest to note that here, as in the catalysis of cinchonine the ratio between rates of conversion in the case of different salts with equal concentrations of organic acid appears to approach a constant, as is shown in Table VI, in which the monohydrochloride is compared with the dihydrochloride.

TABLE VI.

No.	Normality of acetic acid.	Ratio of speed, monohydrochloride: dihydrochloride.
1.....	0.2	$\frac{0.0098}{0.00084} = 11.7$
2.....	0.3	$\frac{0.0138}{0.0012} = 11.5$
3.....	0.8	$\frac{0.0275}{0.0027} = 10.2$
4.....	1.5	$\frac{0.0418}{0.0044} = 9.5$

5. Relation between the Reaction Rates of Cinchonine and Cinchotaxine.—A comparison of the rates of conversion of the two alkaloids in equal concentrations of acid reveals an interesting relation. Since the specific reaction rates obtained in the case of the two alkaloids were not derived in all instances from like concentrations of acid, the comparison in Table VII is naturally confined to the ten examples presenting such identity of concentration. The starred values under K_2' were not determined experimentally, but are calculated from the mean value of $K_2''/K_2' = 1.21$.

From the results set forth in Table VII, it is apparent that the general rate of conversion of cinchonine into cinchotoxine slightly exceeds that of the conversion of the isomeric alkaloid. If we were to assume that the concentration of H^+ ion in solutions of equal concentration with respect to the acid is the same with either alkaloid, then the conditions affecting the catalysis in the two cases must be identical and the mean ratio of 1 : 1.21 would represent a difference of rate due solely to the stereoisomeric difference between the two alkaloids. The significance of this relation will be discussed by the senior author in the following paper.

TABLE VII.

No.	Molality of cinchonidine or cinchonine.	Normality of acetic acid.	Normality of formic acid.	Normality of hydrochloric acid.	K_s' .	K_s'' cinchonine.	K_s''/K_s' .
1.....	0.1	0.2	0.0078	0.0094	1 : 1.20
2.....	0.1	0.3	0.0125	0.0151*	
3.....	0.1	0.4	0.0180	0.0239	1 : 1.27
4.....	0.1	0.5	0.0238	0.0288*	
5.....	0.1	0.8	0.0370	0.0448	1 : 1.21
6.....	0.1	1.5	0.0586	0.0710*	
7.....	0.1	3.0	0.1053	0.1275*	
8.....	0.1	...	0.2	...	0.0050	0.0062	1 : 1.24
9.....	0.1	...	0.3	...	0.0076	0.0092*	
10.....	0.1	...	0.4	...	0.0095	0.0121	1 : 1.27
11.....	0.1	...	0.5	...	0.0113	0.0137*	
12.....	0.09	0.2	...	0.09	0.0098	0.0115	1 : 1.17
13.....	0.09	0.3	...	0.09	0.0138	0.0167*	
14.....	0.09	0.4	...	0.09	0.0170	0.0216	1 : 1.27
15.....	0.09	0.8	...	0.09	0.0275	0.0339	1 : 1.23
16.....	0.09	1.5	...	0.09	0.0418	0.0505*	
17.....	0.1	0.2	...	0.2	0.00084	0.0010	1 : 1.19
18.....	0.1	0.3	...	0.2	0.0012	0.0014*	
19.....	0.1	0.5	...	0.2	0.0018	0.0022*	
20.....	0.1	0.8	...	0.2	0.0027	0.0030	1 : 1.11
21.....	0.1	1.5	...	0.2	0.0044	0.0053*	
Mean, 1 : 1.21 +							

Summary.

1. The rate of the conversion of cinchonidine into cinchotoxine in the presence of organic acids is affected in the same general way as that of the conversion of the stereoisomeric cinchonine. With such acids as acetic and formic increasing concentration of acid effects increase in the speed of conversion.

2. The effect of increasing concentration of H^+ ion, as in the case of cinchonine, is to decrease the speed of the reaction. In solutions of uniform concentration with respect to the cinchonidine (0.1 molal) in the presence of such an acid as acetic, increasing concentration of hydrochloric acid leads to a decrease in the speed of conversion until eventually the reaction ceases.

3. The general rate of conversion of cinchonidine into cinchotoxine is less than that of the stereoisomeric cinchonine under the same conditions of temperature and concentration of acid, the ratio between the mean values of the two rates under the same conditions being 1 : 1.21.

examined with the result, as will appear in the following pages, that the influence upon the reaction rate, both of the concentration of the hydroxyl ion and of that of the undissociated organic acid, has been completely established. It will be shown, indeed, that the specific rate of the reaction with respect to the alkaloid is directly proportional to the concentration of the univalent alkaloid ion and is a direct linear function of the concentration of the undissociated organic acid. Furthermore, the specific catalytic action of three organic acids has been measured as well as the specific variation in speed due to stereoisomerism in the case of cinchonine and cinchonidine.

The results, in addition to their affording a mathematical solution of this remarkable catalysis, are doubly significant in that they fully establish the fact that an undissociated molecule can act as a direct catalytic agent in a homogeneous solution.

2. The Concentration of the H^+ Ion.—Since the H^+ ion inhibits the rate of conversion of a cinchona alkaloid into its toxine, a study of the nature of this retardation, as well as that of the positive catalyzing influence of the organic acid, necessitates a determination of the concentration of this ion or of the function of the ion responsible for the inhibiting action. Of the methods which have been employed for direct measurement of the H^+ ion, a colorimetric one such as that of Salm¹ suggests itself, but this is inferior in point of accuracy to that of the hydrogen electrode which has been used to advantage by a number of investigators. In the study of this catalysis, however, any method of direct measurement is objectionable partly on account of the detail work involved and partly on account of the experimental errors necessarily associated with such measurements. It seemed wiser, consequently, to reduce the determination to a calculation based upon a knowledge of the dissociation constants of the different substances present. While in such a calculation

TABLE I.

*Nonionized cinchonine, Cin. $H_2(OH)_2$	= p
*Univalent cinchonine ion, Cin. HOH^+	= q
Bivalent cinchonine ion, Cin. H_3^{++}	= r
Nonionized organic acid, HAC	= S
Ion of organic acid, Ac^-	= t
Hydroxyl ion, OH^-	= u
Hydrogen ion, H^+	= x
Chloride ion, Cl^-	= c
Total cinchonine	= Cin.
Total organic acid	= Ac

TABLE II.⁴

$(p)h_1$	= $(g)(u)$
$(q)h_2$	= $(r)(u)$
$(S)h_3$	= $(x)(t)$
$(x) + (g) + 2(r)$	= $(t) + (c)$
$(p) + (q) + (r)$	= (Cin.)
$(S) + (t)$	= (Ac)
$(x)(u)$	= h_{H^+}

¹ *Z. physik. Chem.*, 57, 471 (1906).

² Loomis and Acree, *Am. Chem. J.*, 46, 585, 621 (1911); Hildebrand, *This Journal* 35, 847 (1913), and others.

³ The nonionized cinchonine is represented as being in the form of the hydrous.

⁴ Symbols express concentrations in mols per liter.

certain assumptions must be made which are not rigidly correct, but are of minor effect upon the comparative results obtained. If in aqueous solution containing cinchonine, hydrochloric acid and an organic acid, we consider that there is neither cinchonine salt nor hydrochloric acid in an undissociated condition, equilibrium will exist between these substances and the ions given under Table I, and the various relations between these substances and their ions may be formulated in the seven equations given under Table II, in which in all cases as elsewhere in this paper concentrations are expressed in mols per liter.

From Equations 1, 2, 5 and 7.

$$(q) = \frac{(\text{Cin.})}{1 + \frac{k_w}{k_1(x)} + \frac{k_2(x)}{k_w}} \quad (a)$$

$$(r) = \frac{(\text{Cin.})}{1 + \frac{k_w}{k_2(x)} + \frac{k_w^2}{k_1 k_2(x)^2}} \quad (b)$$

From Equations 3 and 6

$$(t) = \frac{k_3(\text{Ac})}{k_3 + (x)} \quad (c)$$

Substituting in Equation 4 the values of q , r and t from Equations a , b and c , we have,

$$(x) = \frac{k_3(\text{Ac})}{k_3 + (x)} + \frac{(\text{Cin.})}{1 + \frac{k_w}{k_1(x)} + \frac{k_2(x)}{k_w}} + \frac{2(\text{Cin.})}{1 + \frac{k_w}{k_2(x)} + \frac{k_w^2}{k_1 k_2(x)^2}} \quad (d)$$

which may be expressed in the general equation:

$$(x) = (x) + (\text{Cin.}) - \frac{k_3(\text{Ac})}{k_3 + (x)} + \frac{(\text{Cin.}) \left(\frac{k_1 k_2(x)^2}{k_w^2} - 1 \right)}{1 + \frac{k_1(x)}{k_w} + \frac{k_1 k_2(x)^2}{k_w^2}} \quad (e)$$

In the absence of hydrochloric acid, this equation takes the form,

$$(\text{Ac}) = \left[(x) + (\text{Cin.}) + \frac{(\text{Cin.}) \left(\frac{k_1 k_2(x)^2}{k_w^2} - 1 \right)}{1 + \frac{k_1(x)}{k_w} + \frac{k_1 k_2(x)^2}{k_w^2}} \right] \left[\frac{k_3 + (x)}{k_3} \right] \quad (f)$$

An equation is thus obtained in which, in solutions of known concentrations with respect to the cinchonine, hydrochloric acid and the organic acid, the concentration of the hydrogen ion is expressed in terms of the dissociation constant of the organic acid (k_3), the first and second dissocia-

tion constants of cinchonine (k_1 and k_2), and the ionization product of water (k_w).

In applying this general equation for calculating the concentration of H^+ ion, it became necessary to determine the values of k_1 , k_2 , k_3 and k_w at 100° , the temperature at which the catalysis was studied.

The value of k_w at 100° as determined by A. A. Noyes¹ is 48×10^{-15} . The value of the dissociation constant of acetic acid (k_a) at this temperature as calculated by the same investigator² from conductivity measurements is 1.11×10^{-5} . The corresponding dissociation constants for formic and propionic acids at 100° have not as yet been experimentally determined. Since the heats of neutralization of the three organic acids named, as determined by Thomsen³ at $18-20^\circ$, closely approach a common value, it was assumed that the ratio of the dissociation constant at 100° to that at a temperature such as 18° , or K_{100}/K_{18} , would be practically constant in the case of the three acids. If the dissociation constants for formic,⁴ acetic⁵ and propionic⁶ acids at 18° are, respectively, 2.14×10^{-4} , 1.82×10^{-5} and 1.4×10^{-5} , the calculated value of this constant at 100° for formic acid will be 1.31×10^{-4} and for propionic acid at the same temperature will be 0.86×10^{-5} . These values which cannot vary much from the true values were used in the calculations made later in this paper.

The so-called first and second dissociation constants of cinchonine, k_1 and k_2 , have been measured by Veley⁷ who obtains at 15° the values $k_1 = 1.63 \times 10^{-7}$ and $k_2 = 3.3 \times 10^{-10}$. The measurement of the first constant was based on the determination of the quantity of sodium hydroxide contained in a hydrolyzed aqueous solution of borax which was required to produce an initial precipitation of alkaloid from an aqueous solution of the hydrochloride and is open to question as to its accuracy. By a conductivity method, another investigator⁸ obtains at 18° the value $k_1 = 1.2 \times 10^{-6}$, which is probably more nearly correct. Veley based his determination of the second dissociation constant on measuring colorimetrically the degree of hydrolysis of cinchonine dihydrochloride in an aqueous solution of known concentration, methyl orange being used as indicator. The same method was later employed by Barratt⁹ in measuring the second dissociation constant of quinine. From an app

¹ Noyes, Kato and Sosman, *THIS JOURNAL*, 32, 159 (1910).

² Noyes, *Ibid.*, 30, 335 (1908).

³ *Thermochemistry*, pp. 93-95 (1908).

⁴ Salin, *Z. physik. Chem.*, 63, 83 (1908); Ostwald, *Ibid.*, 3, 170 (1889).

⁵ Noyes, *THIS JOURNAL*, 30, 335 (1908).

⁶ Barniwater, *J. physik. Chem.*, 45, 557 (1903); 56, 225 (1906).

⁷ *J. Chem. Soc.*, 93, 2114 (1908); 95, 758 (1909).

⁸ Manz, *Dis. Tübingen* (1904).

⁹ Barratt, *Z. Elektrochem.*, 16, 130 (1910).

tion of the method in this laboratory¹ the values of k_2 for cinchonine and cinchonidine at a temperature of 15–18° were found to be, respectively, 0.597×10^{-10} and 0.509×10^{-10} , or practically identical within the limits of experimental error. At a temperature of 100°, cinchonine by the same method gave $k_2 = 1.11 \times 10^{-9}$, the value used for both cinchonine and cinchonidine in the calculations appearing later in this paper.

The value of the first dissociation constant, k_1 , at 100° was not determined, since, as can readily be shown, this constant may be ignored in the calculations made. If for example, k_1 at 100° has a value of not less than 10^{-6} , an assumption which may be safely made as the actual value is doubtless considerably above this, then for all concentrations of hydrogen ion even down to one of the three lowest measured (8.3×10^{-6}) the final fraction in the general equation (e) may be simplified so that this equation becomes,

$$(c) = (x) + (\text{Cin.}) - \frac{k_3(\text{Ac})}{k_3 + (x)} + \frac{k_2(\text{Cin.})(x)}{k_w + k_2(x)}, \quad (g)$$

or, in the absence of hydrochloric acid,

$$(\text{Ac}) = \left[(x) + (\text{Cin.}) + \frac{k_2(\text{Cin.})(x)}{k_w + k_2(x)} \right] \left[\frac{k_3 + (x)}{k_3} \right]. \quad (h)$$

The error introduced by this simplification of the equation is negligible in all concentrations of hydrogen ion calculated, except possibly the three lowest. If, for example, k_1 equals the minimum value of 10^{-6} , the concentration of H^+ ion calculated as 8.0×10^{-6} by Equation *h* will be slightly over 10% too low; and the concentration calculated as 1.06×10^{-6} will be 7% too low. The value calculated as 3.06×10^{-6} H^+ ion will, however, be only slightly over 1% too low and with increasing concentrations, the possible error soon reduces to a fraction of a per cent. Since these results represent the maximum error possible under these conditions, the simplified equations (*g* and *h*) were employed in the calculations of H^+ ion presented in this paper.

3. The Concentrations of the Undissociated Organic Acid and of the Univalent and Bivalent Cinchonine Ions.—The concentration of the H^+ ion having been fixed, that of the undissociated organic acid is readily obtained. By combining Equations 3 and 6, Table II, there is derived the following general equation for calculating this value:

$$(S) = \frac{(\text{Ac})(x)}{(x) + k_3} \quad (i)$$

The concentration of the H^+ ion affords also a ready means of calculating the concentrations of univalent and bivalent cinchonine ions. As has already been pointed out, from the experimental determination of k_2 ,

¹ From unpublished work in this laboratory.

$$\frac{(\text{Cin. H}_2^{++}) \times (\text{OH}^-)}{(\text{Cin. H}^+)} = 1.11 \times 10^{-9}.$$

Since in water at 100°, $(\text{H}^+) \times (\text{OH}^-) = 48 \times 10^{-14}$, the foregoing equation may be expressed as,

$$\frac{(\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)} = \frac{(\text{H}^+)}{4.32 \times 10^{-4}},$$

or

$$\frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)} = \frac{4.32 \times 10^{-4} + (\text{H}^+)}{4.32 \times 10^{-4}},$$

whence,

$$\frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})} = \frac{1}{1 + 2.315 \times 10^3 (\text{H}^+)}, \quad (j)$$

an equation which gives the ratio of univalent cinchonine ion to the total cinchonine in terms of the concentration of the H^+ ion.

In a similar manner, the ratio of the bivalent cinchonine ion to total cinchonine may be derived and expressed as follows:

$$\frac{(\text{Cin. H}_2^{++})}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})} = \frac{2.315 \times 10^3 (\text{H}^+)}{1 + 2.315 \times 10^3 (\text{H}^+)} \quad (k)$$

4. Tabulation of Results.—From the data presented in the foregoing papers on the rates of conversion of cinchonine and of cinchonidine cinchotoxine,¹ were calculated the concentrations of H^+ ion, of non-

ionized organic acid and the value for $\frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$, according to the general equations (g or h, i and j). In the results which are given in Tables III to VII inclusive, K_2 is the rate of conversion; in all of the concentrations of acid, of H^+ ion and of nonionized organic acid are in mols per liter, and the values under $\frac{\text{Cin. H}^+}{\text{Cin. H}^+ + \text{Cin. H}_2^{++}}$ are

ratio of the univalent cinchonine ion to the total cinchonine in the solution.

TABLE III.—CINCHONINE, 0.25 MOLAL.

No.	Acetic acid.	K_2 .	H^+ .	$\frac{\text{Cin. H}^+}{\text{Cin. H}^+ + \text{Cin. H}_2^{++}}$	Acetic acid ionized.
1.....	0.50	0.0192	1.06×10^{-5}	0.976	0.24
2.....	0.75	0.0327	2.07×10^{-5}	0.957	0.40
3.....	1.00	0.0434	3.05×10^{-5}	0.934	0.73
4.....	1.25	0.0566	4.03×10^{-5}	0.915	0.90
5.....	1.50	0.0721	5.15×10^{-5}	0.896	1.23
6.....	2.00	0.0901	6.70×10^{-5}	0.867	1.74
7.....	2.50	0.1112	8.43×10^{-5}	0.838	2.25

¹ Biddle and Brauer, *THIS JOURNAL*, 37, 2065 (1915); Biddle and Butcher, *Ibid.*, 37, 2082 (1915).

TABLE IV.—CINCHONINE, 0.01 MOLAL.

No.	Acetic acid.	Hydrochloric acid.	K_2	H^+ .	Cin. H^+		Acetic acid non-ionised.
					Cin. H^+	+ Cin. H_2^{++} .	
1.....	0.05	...	0.0058	3.99×10^{-5}	0.915		0.0391
2.....	0.10	...	0.0089	8.40×10^{-5}	0.839		0.0883
3.....	0.15	...	0.0127	1.24×10^{-4}	0.779		0.138
4.....	0.20	...	0.0162	1.61×10^{-4}	0.729		0.187
5.....	0.40	...	0.0256	2.98×10^{-4}	0.593		0.386
6.....	0.80	...	0.0347	5.40×10^{-4}	0.445		0.784
7.....	0.5	0.010	0.0163	7.70×10^{-4}	0.360		0.493
8.....	0.5	0.015	0.0114	1.83×10^{-3}	0.240		0.495
9.....	0.5	0.020	0.0056	3.05×10^{-3}	0.125		0.497

TABLE V.—CINCHONINE, 0.1 MOLAL.

No.	Acetic acid.	Hydrochloric acid.	K_2	H^+ .	Cin. H^+		Acetic acid non-ionised.
					Cin. H^+	+ Cin. H_2^{++} .	
1	0.15	...	0.00565	5.30×10^{-5}	0.988		0.0485
2	0.175	...	0.00712	8.00×10^{-5}	0.985		0.0734
3	0.20	...	0.0094	1.06×10^{-4}	0.976		0.0977
4	0.40	...	0.0239	3.06×10^{-4}	0.937		0.294
5	0.80	...	0.0448	6.73×10^{-4}	0.868		0.688
6	1.00	...	0.0566	8.45×10^{-4}	0.837		0.884
7	1.70	...	0.0796	1.40×10^{-3}	0.756		1.574
8	2.00	...	0.0901	1.63×10^{-3}	0.729		1.870
9	3.20	...	0.1351	2.49×10^{-3}	0.636		3.075
10	4.00	...	0.1486	3.03×10^{-3}	0.590		3.870
11	8.00	...	0.2229	5.56×10^{-3}	0.438		7.850
12	1.00	0.100	0.0389	2.74×10^{-4}	0.613		0.962
13	1.00	0.125	0.0321	4.30×10^{-4}	0.501		0.975
14	1.00	0.150	0.0227	7.60×10^{-4}	0.362		0.986
15	1.00	0.175	0.0140	1.70×10^{-3}	0.203		0.994
16	1.00	0.200	0.0044	7.20×10^{-3}	0.057		0.998
17	1.00	0.210	0.0021	1.37×10^{-2}	0.031		0.999
18	1.00	0.220	0.0015	2.22×10^{-2}	0.019		1.000
19	1.00	0.230	0.0011	3.17×10^{-2}	0.014		1.000
20	0.5	0.15	0.0136	6.05×10^{-4}	0.418		0.491
21	0.5	0.25	0.00035	5.09×10^{-3}	0.0085		0.500
22	0.1	0.09	0.0076	7.30×10^{-5}	0.859		0.0868
23	0.2	0.09	0.0115	1.12×10^{-4}	0.796		0.182
24	0.4	0.09	0.0216	1.66×10^{-4}	0.724		0.374
25	0.8	0.09	0.0339	2.53×10^{-4}	0.632		0.767
26	1.6	0.09	0.0548	4.00×10^{-4}	0.520		1.552
27	0.1	0.20	0.00066	6.40×10^{-3}	0.0634		0.0999
28	0.2	0.20	0.0010	6.45×10^{-3}	0.0630		0.199
29	0.4	0.20	0.0017	6.70×10^{-3}	0.0607		0.399
30	0.8	0.20	0.0030	6.94×10^{-3}	0.0587		0.799
31	2.0	0.20	0.0068	7.90×10^{-3}	0.052		1.995
32	2.0	0.30	0.0000	1.01×10^{-1}	0.0043		2.000

¹In the experiments whose results are recorded under 22 to 26 inclusive, the concentration of the cinchonine was 0.09 molal.

TABLE VI.—CINCHONINE, 0.1 MOLAL.

No.	Propionic acid.	Formic acid.	Hydrochloric acid.	K_s .	H^+ .	Cin. H^+ .		Organic acid non-ionised.
						Cin. H^+ + Cin. H_s^{++}		
1	0.20	0.0117	8.30×10^{-4}	0.985		0.0985
2	0.40	0.0296	2.40×10^{-3}	0.949		0.294
3	0.80	0.0611	5.33×10^{-3}	0.890		0.690
4	1.20	0.0760	8.10×10^{-3}	0.844		1.085
5	..	0.2	...	0.0062	9.20×10^{-4}	0.825		0.0826
6	..	0.4	...	0.0121	2.51×10^{-3}	0.634		0.263
7	..	0.8	...	0.0165	5.40×10^{-3}	0.445		0.644
8	0.15	0.00163	4.25×10^{-4}	0.505		..
9	0.175	0.00077	1.205×10^{-3}	0.264		..
10	0.20	0.0003	6.46×10^{-3}	0.063		..
11	0.25	0.0001	5.08×10^{-3}	0.0085		..
12	0.40	0.0000

TABLE VII.—CINCHONIDINE, 0.1 MOLAL.

No.	Acetic acid.	Formic acid.	Hydrochloric acid.	K_s .	H^+ .	Cin. H^+ .		Organic acid non-ionised.
						Cin. H^+ + Cin. H_s^{++}		
1	0.2	0.0078	1.06×10^{-3}	0.976		0.0977
2	0.3	0.0125	2.06×10^{-3}	0.956		0.195
3	0.4	0.0180	3.06×10^{-3}	0.937		0.294
4	0.5	0.0238	4.00×10^{-3}	0.915		0.391
5	0.8	0.0370	6.73×10^{-3}	0.868		0.688
6	1.5	0.0586	1.25×10^{-2}	0.775		1.378
7	3.0	0.1053	2.35×10^{-2}	0.648		2.860
8 ¹	0.2	...	0.09	0.0098	1.12×10^{-3}	0.796		0.182
9 ¹	0.3	...	0.09	0.0138	1.40×10^{-3}	0.755		0.278
10 ¹	0.4	...	0.09	0.0170	1.66×10^{-3}	0.724		0.374
11 ¹	0.8	...	0.09	0.0275	2.53×10^{-3}	0.632		0.767
12 ¹	1.5	...	0.09	0.0418	3.81×10^{-3}	0.531		1.456
13	0.2	...	0.2	0.0008	6.45×10^{-3}	0.0630		0.199
14	0.3	...	0.2	0.0012	6.57×10^{-3}	0.0617		0.299
15	0.5	...	0.2	0.0018	6.78×10^{-3}	0.0600		0.499
16	0.8	...	0.2	0.0027	6.94×10^{-3}	0.0587		0.799
17	1.5	...	0.2	0.0044	7.53×10^{-3}	0.0543		1.499
18	0.8	...	0.3	0.0000
19	...	0.2	..	0.0050	9.20×10^{-4}	0.825		0.0826
20	...	0.3	..	0.0076	1.72×10^{-3}	0.715		0.170
21	...	0.4	..	0.0095	2.51×10^{-3}	0.634		0.263
22	...	0.5	..	0.0113	3.25×10^{-3}	0.570		0.356

5. Relation between the Speed of the Reaction and the Concentration of H^+ Ion.—If,—from Table V in those experiments in which the concentration of the acetic acid is 1.0 molal and the concentration of H^+ ion is varied by the introduction of increasing quantities of hydrochloric acid (Table V, 12-19),—the concentration of H^+ ion is plotted against the reaction velocities, we obtain the curve (I) given in Fig. 1. If now the speed of the

¹ In the experiments whose results are recorded under 8 to 12 inclusive, the concentration of the cinchonidine was 0.09 molal.

reaction were directly proportional to the total organic acid present, this curve, the concentration of organic acid being constant, would represent the influence of H^+ ion upon the reaction velocity. That the reaction velocity is not directly proportional to the concentration of the total organic acid, appears from a consideration of the rates of conversion

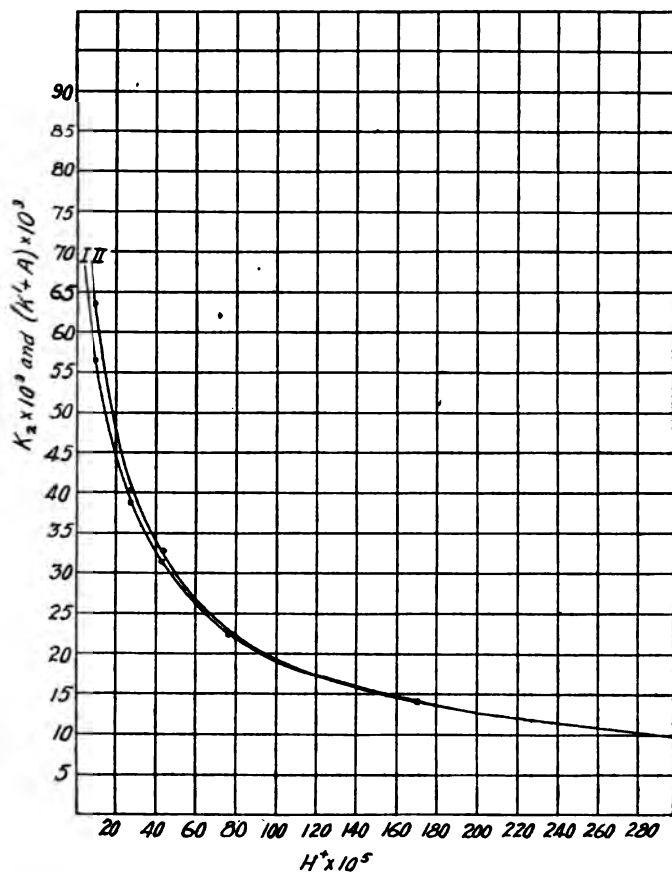


Fig. 1.

of cinchonine into cinchotoxine already presented.¹ The reaction velocity appears rather to be a function of the concentration of the undissociated acid as has previously been pointed out² and if a linear function, then the specific reaction rate, K , may for a given concentration of H^+ ion be expressed by the equation,

$$K = K' + AC', \quad (1)$$

¹ Biddle and Brauer, *Loc. cit.*

² Biddle, *Ber.*, 45, 2832 (1912).

where K' and A are constants and C' is the concentration of the undissociated organic acid in mols per liter.¹

If now the values of K' are known for the various concentrations of H^+ ion studied, the value $K' + A$ is the reaction rate at molal concentration of the *undissociated* organic acid. This rate, plotted against the concentration of H^+ ion, should give a graph expressing the interrelation of these two values freed from other influences. The values of K' at varying concentrations of H^+ ion, may be obtained from a study of the conversion of cinchonine in the presence of hydrochloric acid alone. The rate of conversion in the presence of this acid is small and if we assume that the hydrochloric acid itself has no positive catalytic effect, as indicated below, then the rates at varying concentration of H^+ ion are in this case really the values of K' at these concentrations. As shown in Fig. 2 (Section 6) these rates of conversion, or the values of K' , are to be considered as a linear function of $\frac{\text{Cin. } H^+}{\text{Cin. } H^+ + \text{Cin. } H_2^{++}}$. Introducing in

Table VIII the values of K' as obtained from Fig. 2, we derive the corresponding values of $K' + A$, in which the concentration of undissociated organic acid is constant. Graph II in Fig. 1 results from the plotting of $K' + A$ against the concentration of H^+ ion. It will be observed that the curve obtained, except in the lower concentrations of H^+ ion, coincides with that resulting from the use of the original reaction velocities, K_2 .

TABLE VIII.
Cinchonine, 0.1 molal. Acetic acid, 1.0 molal.

No.	Hydrochloric acid.	H^+ .	K_2 .	K' .	$K_2 - K'$.	A .	$K' + A$.
1	...	8.45×10^{-3}	0.0566	0.00270	0.0539	0.0610	0.0637
2	0.100	2.74×10^{-4}	0.0389	0.00197	0.0369	0.0384	0.0404
3	0.125	4.30×10^{-4}	0.0321	0.00161	0.0305	0.0313	0.0329
4	0.150	7.60×10^{-4}	0.0227	0.00117	0.0215	0.0218	0.0230
5	0.175	1.70×10^{-3}	0.0140	0.00064	0.0134	0.0135	0.0141
6	0.200	7.20×10^{-3}	0.0044	0.00018	0.0042	0.0042	0.0044
7	0.210	1.37×10^{-3}	0.0021	0.00009	0.00201	0.00201	0.0021
8	0.220	2.22×10^{-3}	0.0015	0.00006	0.00144	0.00144	0.0015
9	0.230	3.17×10^{-3}	0.0011	0.00004	0.00106	0.00106	0.0011

6. Relation of the Speed of the Reaction to the Concentration of the Univalent Cinchonine Ion.—If in those experiments in which the total acetic acid is of uniform concentration (1.0 molal), a comparison is made between the specific reaction rates (K_2) and the concentrations of the univalent cinchonine ion (Cin. H^+), a remarkable relationship is discovered. A cursory inspection of the two sets of values in Table IX leads to the conclusion that the reaction velocity is in all probability directly proportional to the concentration of the univalent cinchonine

¹ Biddle and Rosenstein, THIS JOURNAL, 35, 425 (1913).

ion. In order, however, that a study of the matter may be made under conditions of equal concentration with respect to the undissociated organic acid, it becomes necessary to compare with the concentrations of Cin. H^+ ion, not the values of $K_2 = K' + AC'$, but those of $K_2 = K' + A$, in which C' has been reduced to unity. Assuming that the specific reaction rate is proportional to the concentration of the univalent cinchonine ion, then in the equation, $K_2 = K' + AC'$, (K') and (AC') will each be linear functions of this concentration. If, now, in the conversion of cinchonine into cinchotoxine in the presence of hydrochloric acid, this acid is considered to have no positive catalyzing influence, a conclusion which is reached from a consideration of the specific reaction rate in the presence of this acid alone, then in this case, $K_2 = K'$, and the values of K' at varying concentrations of H^+ ion are obtained by plotting the rates (K_2) against the values of $\frac{\text{Cin. H}^+}{\text{Cin. H}^+ + \text{Cin. H}_2^{++}}$, as shown in Fig. 2.

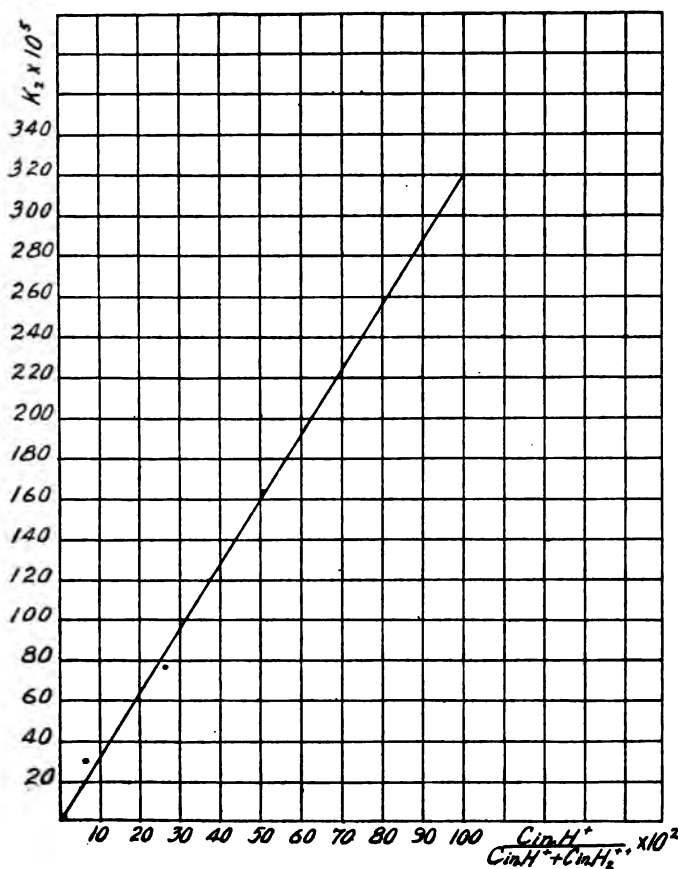


Fig. 2.

TABLE IX.
 Cinchonine, 0.10 molar.

No.	Acetic acid.	Hydrochloric acid.	K_2	$K' + A$	Cin. H^+ .	$\frac{\text{Cin. } H^+}{K' + A}$.
1.....	0.20	...	0.0094	0.0673	0.0976	1.45
2.....	1.00	...	0.0566	0.0637	0.0837	1.31
3.....	1.00	0.100	0.0389	0.0404	0.0613	1.52
4.....	1.00	0.125	0.0321	0.0329	0.0501	1.52
5.....	1.00	0.150	0.0227	0.0230	0.0362	1.57
6.....	1.00	0.175	0.0140	0.0141	0.0203	1.44
7.....	1.00	0.200	0.0044	0.0044	0.0057	1.30
8.....	1.00	0.210	0.0021	0.0021	0.00306	1.46
9.....	1.00	0.220	0.0015	0.0015	0.00191	1.33
10.....	1.00	0.230	0.0011	0.0011	0.00137	1.25 ¹
Mean,						1.433

In Table IX, as in Table VIII, the values under $K' + A$ (obtained from $K' + A = K' + 1/C'(K_2 - K')$) represent the specific reaction rate at constant concentration with respect to the undissociated organic acid. The ratio of the concentration of the univalent cinchonine ion to this rate, $\frac{(\text{Cin. } H^+)}{K' + A}$, is seen to be practically constant in solutions of uniform concentration with respect to the alkaloid.

From these considerations the conclusion must be drawn that, in solutions of uniform concentration with respect to the alkaloid, the speed of the conversion of cinchonine into cinchotoxine at constant concentrations of the undissociated catalyzing acid is directly proportional to the concentration of the univalent cinchonine ion.

As has been pointed out in the previous papers, if the reaction is monomolecular with respect to the alkaloid, then the rate of the reaction for any particular strength of the catalyzer is expressed by the equation:

$$-\frac{d(C)}{dt} = K_2(C)$$

where C is the concentration of the alkaloid at the time t and K_2 is the specific reaction rate. Since, however, the speed of the conversion under the conditions given is directly proportional not to the concentration of the cinchonine, but to that of the univalent cinchonine ion, this equation takes the form,

$$-\frac{d(C)}{dt} = K_2 \frac{(\text{Cin. } H^+)}{(\text{Cin. } H^+) + (\text{Cin. } H_2^{++})} (C),$$

in which $\frac{(\text{Cin. } H^+)}{(\text{Cin. } H^+) + (\text{Cin. } H_2^{++})}$ represents the fraction of the alkaloid in the form of the univalent ion. Now the value of this fraction, is determined by the concentration of the H^+ ion. In any particular solution,

¹ Omitted in calculating mean value, since K_2 at higher concentrations of H^+ ion is open to much larger experimental error.

consequently, in which the concentration of the H^+ ion is assumed to remain unchanged throughout the reaction, the value of this fraction must be constant.

It follows, therefore, that in the values of the specific reaction rate as previously calculated from the experimental data, in any particular case,

$$K_2 = K_0 \frac{(\text{Cin. } H^+)}{(\text{Cin. } H^+) + (\text{Cin. } H_2^{++})}$$

where K_0 is the specific reaction rate which would be observed under the conditions of the experiment in case all of the cinchonine, at any moment, were in the form of the univalent cinchonine ion.

7. Relation of the Speed of the Reaction to the Concentration of the Undissociated Organic Acid.—The specific reaction rate of the conversion of cinchonine to cinchotoxine was determined by Biddle and Rosenstein for two concentrations of acetic acid. In these two instances the reaction velocity was apparently a linear function of the concentration of the organic acid above the diacetate. It was at the time assumed that this concentration represented that of the undissociated acid, an assumption whose error did not appear in the high concentrations employed, but is clearly seen from the data already given in the present paper. The assumption made, however, in the paper referred to and in a previous paper, that the speed of the reaction is a direct function of the concentration of the undissociated organic acid has proved correct.

In the equation, $K_2 = K' + AC'$, it has been shown in the cases considered (Table IX) that $(K' + A) \propto (\text{Cin. } H^+)$, or taking the mean value of 1.433 for the ratio, $\frac{(\text{Cin. } H^+)}{K' + A}$, then $K' + A = 0.697 (\text{Cin. } H^+)$.

This expressed in terms of the ratio of the univalent cinchonine ion to the total cinchonine present gives, since we are working with 0.1 molal cinchonine, the equation,

$$K' + A = 0.0697 \frac{(\text{Cin. } H^+)}{(\text{Cin. } H^+) + (\text{Cin. } H_2^{++})}$$

If now all the cinchonine were converted into the univalent ion, $K' + A$ would become constant, $K_0' + A_0$. Under these conditions,

$$(K' + A) \frac{(\text{Cin. } H^+) + (\text{Cin. } H_2^{++})}{(\text{Cin. } H^+)} = K_0' + A_0 = 0.0697. (m)$$

The value, $K_0' + A_0$, is obviously the specific reaction rate of 0.1 molal cinchonine in acetic acid under conditions under which the concentration of the univalent ion is 0.1 molal and that of the undissociated organic acid is 1.0 molal. From this value, which may be termed the *absolute reaction rate* in the case of 0.1 molal cinchonine in the presence of acetic acid,

$$A_o = 0.0697 - K_o' = 0.0665 \quad (\pi)$$

since from Fig. 2 the value of $K_o' = 0.0032$.

The relation of A_o to K_s will be seen from the general equation,

$$K_s = K' + AC' = (K_o' + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})} \quad (o)$$

in which K' and A are the constants in the equation, $K_s = K' + AC'$, at any constant concentration of univalent cinchonine ion and K_o' and A_o are the corresponding constants under conditions under which all the cinchonine is in the form of the univalent ion.

From the above equation,

$$A_o = 1/C' \left[K_s \frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)} - K_o' \right]. \quad (p)$$

Since, in the absence of the catalyzing organic acid,

$$K_o' = K' \frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)},$$

the last equation may also be written,

$$A_o = 1/C' (K_s - K') \frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)}. \quad (q)$$

The value of K' for any value of univalent cinchonine ion may be obtained from the graph, Fig. 2, or calculated directly from the equation,

$$K' = K_o' \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}. \quad (r)$$

From these considerations it will be clear that the constancy of the value A_o , as derived from experiments of widely divergent concentrations of organic acid and of H^+ ion, is conditioned upon the correctness of the assumptions that the rate of this conversion is a linear function of the concentration of the undissociated organic acid and is also directly proportional to the concentration of the univalent cinchonine ion. The validity of the assumption with respect to the organic acid will naturally be tested most rigorously in the case of low concentrations of the undissociated acid in which case any error in the assumption must lead to widely divergent values of A_o .

In Table X are brought together the values of A_o as calculated by Equation p for all the cases studied containing acetic acid in which the concentration of the cinchonine was 0.1 molal. The series presents a range of concentration of H^+ ion varying from 5.3×10^{-6} to 1.01×10^{-1} and of concentration of undissociated organic acid varying from 0.0485 molal to 7.85 molal. In all cases, as is seen, A_o is practically a constant within the limits of experimental error and errors introduced by unavoidable assumptions in the calculations. The mean value of A_o as obtained from the thirty-one determinations agrees, as will be seen, with

the mean value already derived under (n) from nine determinations in Table IX.

Under $K' + AC'$ are given the values for K_s as calculated from the equation.

$$K_s = K' + AC' = (K'_o + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_3^{++})} =$$

$$(0.0032 + 0.0665 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_3^{++})}$$

in which the mean value of $A_o = 0.0665$ is employed. The agreement of the calculated values $K' + AC'$ with the measured speeds K_s , as is seen, is fully within the limits of experimental error.

TABLE X.
Cinchonine, 0.10 molal.

No.	Acetic acid.	Hydrochloric acid.	Cin. H ⁺		A _o .	K' + AC'. (K _s , calculated.)	K _s (observed).
			Cin. H ⁺	+ Cin. H ₃ ⁺⁺			
1	0.15	...	0.988		0.0522	0.00634	0.00565
2	0.175	...	0.985		0.0550	0.00795	0.00712
3	0.20	...	0.976		0.0655	0.00945	0.0094
4	0.40	...	0.937		0.0738	0.0213	0.0239
5	0.80	...	0.868		0.0790	0.0425	0.0448
6	1.00	...	0.837		0.0731	0.0519	0.0566
7	1.70	...	0.756		0.0645	0.0816	0.0796
8	2.00	...	0.729		0.0645	0.0928	0.0901
9	3.20	...	0.636		0.0680	0.1320	0.1351
10	4.00	...	0.590		0.0644	0.1540	0.1486
11	8.00	...	0.438		0.0650	0.2290	0.2229
12	1.00	0.100	0.613		0.0627	0.0411	0.0389
13	1.00	0.125	0.501		0.0624	0.0342	0.0321
14	1.00	0.150	0.362		0.0601	0.0249	0.0227
15	1.00	0.175	0.203		0.0667	0.0141	0.0140
16	1.00	0.200	0.057		0.0742	0.0040	0.0044
17	1.00	0.210	0.0306		0.0655	0.00204	0.0021
18	1.00	0.220	0.0191		0.0754	0.00123	0.0015
19	1.00	0.230	0.0137		0.0773	0.00096	0.0011
20	0.5	0.15	0.418		0.0622	0.0150	0.0136
21	0.5	0.25	0.0085		0.0760	0.0003	0.00035
22	0.1	0.09	0.859		0.0654	0.0077	0.0076
23	0.2	0.09	0.796		0.0620	0.0121	0.0115
24	0.4	0.09	0.724		0.0711	0.0202	0.0216
25	0.8	0.09	0.632		0.0640	0.0342	0.0339
26	1.6	0.09	0.520		0.0655	0.0554	0.0548
27	0.1	0.20	0.063		0.0761	0.00062	0.00066
28	0.2	0.20	0.063		0.0640	0.00103	0.0010
29	0.4	0.20	0.061		0.0622	0.0018	0.0017
30	0.8	0.20	0.059		0.0600	0.0033	0.0030
31	2.0	0.20	0.052		0.0640	0.0071	0.0068
32	2.0	0.30	0.0043		0.0000

Mean, 0.0665

Closer agreement apart from experimental error could scarcely be expected in view of the fact that small errors are necessarily introduced into the calculation by ignoring such conditions as the presence of undissociated cinchonine salt and of undissociated hydrochloric acid, such conditions also as the slight alteration in concentration of H^+ ion due to the change of cinchonine to cinchotoxine of slightly different basicity, and such also as the fact that with increasing concentration of organic acid the dissociation constant of the acid itself changes. At constant concentration with respect to the cinchonine, however, the errors introduced by these factors must, from the very nature of the case, be so small as to be negligible with reference to any serious effect upon the final results. It is, consequently, conclusively established that *the rate of conversion of cinchonine into cinchotoxine under the conditions given is directly proportional to the concentration of the univalent cinchonine ion and is a linear function of the concentration of the undissociated organic acid.*

8. The Specific Catalytic Action of Different Organic Acids.—Since the absolute reaction rate, A_0 , for acetic acid represents the specific reaction rate for one mol of undissociated organic acid, this value when determined for different organic acids affords a comparison of the specific catalytic action of these acids under like conditions. In Table XI are given the calculated values of A_0 and of $K' + AC'$ for formic and propionic acids. As is seen, the same general principles obtain as are found in the case of acetic acid. The mean value of A_0 for formic acid equals 0.0550, that for propionic acid 0.0901, and as already shown that for acetic acid is 0.0665. The specific catalytic action of the acid would seem then to increase with acids of decreasing dissociation constant.

TABLE XI.
Cinchonine, 0.1 molar.

No.	Formic acid.	Propionic acid.	Cin. H^+	A_0 .	$K' + AC'$. (K_1 calculated.)	K_2 (observed).
			Cin. $H^+ + Cin. H_2^{++}$.			
1.....	0.2	...	0.825	0.0524	0.00642	0.0062
2.....	0.4	...	0.634	0.0605	0.0113	0.0121
3.....	0.8	...	0.445	0.0527	0.0173	0.0165
4.....	...	0.2	0.985	0.0885	0.0119	0.0117
5.....	...	0.4	0.949	0.0960	0.0280	0.0296
6.....	...	0.8	0.890	0.0952	0.0580	0.0611
7.....	...	1.2	0.844	0.0818	0.0846	0.0760
Formic acid, A_0			= 0.0550			
Acetic acid, A_0			= 0.0665			
Propionic acid, A_0			= 0.0901			

¹ This assumption would, of course, be incorrect if the undissociated cinchonine salts varied greatly in solutions of constant initial concentration with respect to the cinchonine and if at the same time the reaction rate were largely influenced by the concentration of such undissociated salt. As indicated later in this article, these factors will be considered in a subsequent paper.

TABLE XII.

	A_0/A_0	M. W./M. W.
Propionic/Acetic.....	1.35	1.23
Acetic/Formic.....	1.21	1.3
Propionic/Formic.....	1.64	1.61

p. The Effect upon the Reaction Rate of Varying the Concentration of the Cinchonine.—If the reaction in the conversion of cinchonine into echotoxine is monomolecular with respect to the alkaloid, the specific reaction rate K_2 , should be independent of the *initial* concentration of the cinchonine. It is of interest, consequently, to determine the value of A_0 (the absolute reaction rate of an organic acid) for the two other concentrations of cinchonine studied, *viz.*, 0.25 and 0.01 molal. A general consideration of the specific reaction rates (K_2), measured in the case of 0.25, 0.1, and 0.01 molal cinchonine, leads one to infer that there is a general decrease in speed with increasing initial concentration of cinchonine. This inference is substantiated in comparing the values of A_0 .

TABLE XIII.
Cinchonine, 0.25 molal.

No.	Acetic acid.	Cin. H ⁺		A _o .	K' + AC'. † (K _s calculated.)	K _s (observed).
		Cin. H ⁺ + Cin. H ₂ ⁺⁺				
1.....	0.50	0.976		0.0676	0.0178	0.0192
2.....	0.75	0.957		0.0633	0.0319	0.0327
3.....	1.00	0.934		0.0590	0.0450	0.0434
4.....	1.25	0.915		0.0600	0.0580	0.0566
5.....	1.50	0.896		0.0628	0.0706	0.0721
6.....	2.00	0.867		0.0588	0.0939	0.0901
7.....	2.50	0.838		0.0587	0.1169	0.1112
				Mean,	0.0615	

TABLE XIV.
Cinchonine, 0.01 molal.

No.	Acetic acid.	Hydrochloric acid.	Cin. H ⁺	A ₀ .	K' + AC' (K _s calculated.)	K _s (observed.)
			Cin. H ⁺ + Cin. H ₂ ⁺⁺			
1.....	0.05	...	0.915	0.0805	0.0062	0.0058
2.....	0.10	...	0.839	0.0840	0.0094	0.0089
3.....	0.15	...	0.779	0.0955	0.0118	0.0127
4.....	0.20	...	0.729	0.1015	0.0147	0.0162
5.....	0.40	...	0.593	0.1033	0.0228	0.0256
6.....	0.80	...	0.445	0.0955	0.0332	0.0347
7.....	0.50	0.010	0.360	0.0860	0.0173	0.0163
8.....	0.50	0.015	0.240	0.0895	0.0116	0.0114
9.....	0.50	0.020	0.125	0.0842	0.0061	0.0056
Mean.				0.0911		

In Tables XIII and XIV the values of A_0 and of $K' + AC'$ have been calculated for the various measurements made in solutions containing 0.25 and 0.01 molal cinchonine. In these calculations, as in those previously determined, it is assumed that $K_0' = 0.0032$. On considering the values obtained it is evident that for a given concentration of cinchonine A_0 as before approaches a constant. The mean constant resulting, however, varies with the concentration of the alkaloid. Thus, for solutions containing, respectively, 0.25, 0.1 and 0.01 molal cinchonine, the mean values of A_0 are 0.0615, 0.0665 and 0.0911.

In seeking some explanation of these deviations of the values of A_0 from constancy, one naturally raises the question as to whether similar variations have been observed in such catalyses as the inversion of cane sugar. The question must be answered in the affirmative; for, as Ostwald¹ has shown, the rate of inversion is strictly proportional to the concentration of the H^+ ions *only* when the solutions are *dilute*, since at higher concentrations deviations occur. The variations in the values of A_0 are, consequently, not abnormal.

The actual cause of these deviations is more difficult to determine. Certain factors, may however, be noted. In the determination of the concentration of H^+ ion, upon which all subsequent calculations in this paper depend, no account has been taken of the existence in the solution of nonionized cinchonine salt. That such salt exists can not be questioned. The concentration of undissociated salt, though probably small, may be assumed not to vary greatly in solutions of constant concentration with respect to the alkaloid, but to increase in solutions of increasing concentration with respect to the cinchonine. The general effect of this factor might not be noticeable in solutions of constant concentration with respect to the alkaloid, but would probably lead to an apparent decrease in the value of A_0 in solutions of increasing concentration with respect to this substance, unless the undissociated salt exerted an effect upon the reaction velocity exceeding that of the univalent cinchonine ion. As is seen, the deviations in the values of A_0 for the three concentrations of cinchonine studied are in the direction which would naturally be expected from the presence of undissociated cinchonine salt. It is of interest to note that if the variations in the value of A_0 could be attributed *solely* to the varying proportion of undissociated salt, these might serve as a basis for calculating in any case the amount of alkaloid in the form of such salt.

Another factor which the calculation of necessity ignores is the effect upon the reaction rate of the varying total concentration of the salt, in other words, the salt effect. The "neutral salt effect," which in other cases

¹ *J. prakt. Chem.*, [2] 31, 307 (1885).

of catalysis has been the subject of numerous investigations,¹ would in different concentrations of cinchonine salt naturally affect the value of A_0 . The whole question of the salt effect, however, is involved with that of the undissociated salt which, as will be shown later in this paper, must be taken into consideration in a complete interpretation of the mechanism of the reaction.

An interesting attempt has been made by Rosanoff² to account in general for unexpected variations in catalytic reaction rates due to changes in concentration. He divides catalyzers into two classes, direct and indirect. The former are assumed to take part in the reaction, but not to appear in the stoichiometric equation; the latter "without taking any part in the reaction are regarded as influencing its velocity by affecting the particular conditions upon which the mechanism of the given reaction may depend." Under this classification as he has noted, "all substances are indirect catalyzers of *all* reactions." It is too early as yet, however, to determine just what value is to be assigned to the general equation which he has developed.

10. The Specific Reaction Rate of the Stereoisomeric Cinchonidine.—

In studying the exact catalytic action of organic acids upon the isomeric cinchonidine, it becomes necessary, as in the case of cinchonine, to determine the values of the dissociation constants of the alkaloid. As has already been shown earlier in this paper, the values of the second dissociation constant, k_2 , are practically identical in the case of the two alkaloids. As to the first dissociation constant, k_1 , the results obtained by Veley³ indicate but slight difference in the two cases. While, as has already been pointed out the accuracy of Veley's method is open to question, it may at least be safely concluded that the difference between the values of k_1 in the two alkaloids, if at all existent, must be small. In determining the concentration of H^+ ion, consequently, the dissociation constant k_1 , as has already been pointed out, may be neglected as was done in the case of cinchonine. The data presented in Table VII were calculated accordingly in the same way as those given in the preceding tables.

In the preceding paper⁴ attention was called to the fact that the mean ratio between the specific reaction rates of cinchonidine and cinchonine under like conditions is that of 1 : 1.21+. The significance of this ratio becomes apparent, if the first and second dissociation constants, k_1 and k_2 , of the two alkaloids possess for all practical purposes identical values. Then, the concentration of H^+ ion and that of undissociated organic acid

¹ See references in introduction of this paper.

² THIS JOURNAL, 35, 173, 248 (1913).

³ J. Chem. Soc., 95, 758 (1909).

⁴ Biddle and Butzbach, THIS JOURNAL, 37, 2082 (1915).

will remain unchanged under like conditions whether the solution contain cinchonine or cinchonidine and any constant difference in speed of conversion must be explained on the basis of stereoisomeric difference existing between the two alkaloids.

In Table XV is presented a study of all the reaction rates given in Table VII. The values under $K' + AC'$ were calculated from the equation,

$$K' + AC' = (K' + A_0 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})} = \frac{(0.0032 + 0.0665 C') (\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

They represent, consequently, the specific reaction rates for cinchonidine under the conditions given and serve as a basis of comparison with experimental values of K_2 for cinchonidine under like conditions.

TABLE XV.
Cinchonidine, 0.1 molal.

Cinchonidine, 0.1 molar.

No.	Normality of organic acid. <i>Acetic acid.</i>	Normality of hydrochloric acid.	K_2 (observed cinchonidine).	$K' + AC'$ (K_2 , calculated, cinchonine.)	$\frac{K' + AC'}{K_2}$	A_0' (cinchonidine).	A_0'' (cinchonine).
1.....	0.2	..	0.0078	0.0095	1.21	0.0550	0.0665
2.....	0.3	..	0.0125	0.0155	1.24	0.0535	0.0646
3.....	0.4	..	0.0180	0.0213	1.18	0.0563	0.0680
4.....	0.5	..	0.0238	0.0267	1.12	0.0596	0.0725
5.....	0.8	..	0.0370	0.0425	1.15	0.0580	0.0704
6.....	1.5	..	0.0586	0.0735	1.25	0.0531	0.0644
7.....	3.0	..	0.1053	0.1251	1.19	0.0560	0.0677
8 ¹	0.2	0.09	0.0098	0.0121	1.24	0.0529	0.0644
9 ¹	0.3	0.09	0.0138	0.0164	1.19	0.0563	0.0682
10 ¹	0.4	0.09	0.0170	0.0202	1.19	0.0557	0.0676
11 ¹	0.8	0.09	0.0275	0.0342	1.24	0.0531	0.0644
12 ¹	1.5	0.09	0.0418	0.0531	1.27	0.0521	0.0630
13.....	0.2	0.2	0.0008	0.0010	1.25	0.0505	0.0615
14.....	0.3	0.2	0.0012	0.0014	1.17	0.0560	0.0680
15.....	0.5	0.2	0.0018	0.0022	1.22	0.0548	0.0666
16.....	0.8	0.2	0.0027	0.0033	1.22	0.0543	0.0657
17.....	1.5	0.2	0.0044	0.0056	1.27	0.0523	0.0634
<i>Formic acid.</i>					Mean,	0.0547	0.0663
18.....	0.2	..	0.0050	0.0064	1.28	0.0414	0.0500
19.....	0.3	..	0.0076	0.0090	1.18	0.0469	0.0566
20.....	0.4	..	0.0095	0.0113	1.19	0.0470	0.0570
21.....	0.5	..	0.0113	0.0130	1.15	0.0482	0.0585
					Mean,	1.21	0.0459

The ratio between these two values, or $\frac{K' + AC'}{K_2}$, should be identical with that previously obtained, *viz.*, 1 : 1.21+. As will be noted the

¹ The concentration of the cinchonidine in these experiments was 0.09 molal.

ting mean value of all the ratios is, $\frac{K' + AC'}{K_2} = 1.21$, a value which practically identical with that previously given. The general specific reaction rate of cinchonine is, consequently, 1.21 times that of cinchonidine under the same experimental conditions. In view of the values obtained for the first and second dissociation constants of the two alkaloids this difference in rate of conversion must be ascribed, as already pointed out, to the stereoisomeric difference between cinchonine and cinchonidine. In the conversion of cinchonine into cinchotoxine (see Equation 6)

$$K_2 = (K_o' + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

in the presence of acetic acid this becomes,

$$K_2 = (0.0032 + 0.0665 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

in the presence of formic acid (see Table XI)

$$K_2 = (0.0032 + 0.0550 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

in the conversion of cinchonidine into cinchotoxine, the general equation naturally becomes,

$$K_2 = \frac{1}{1.21} (K_o' + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})} \quad (5)$$

in the presence of acetic acid this leads to,

$$K_2 = (0.00264 + 0.0550 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

in the presence of formic, to

$$K_2 = (0.00264 + 0.0455 C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

In the case of cinchonidine, then, $K_o' = 0.00264$, for acetic acid $A_o = 0.0665$ and for formic acid $A_o = 0.0550$.

Under A_o' (cinchonidine), Table XV, the values for the absolute reaction rate for cinchonidine have been calculated from the equation,

$$A_o' = 1/C' (K_2 \times \frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)} - 0.00264).$$

For A_o' (cinchonine), the corresponding values for cinchonine have been calculated from the equation,

$$A_o' = 1/C' (1.21 \times K_2 \times \frac{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}{(\text{Cin. H}^+)} - 0.0032).$$

It was of course to be expected, the mean values obtained for A_o' and K_2 correspond with those already given, as is shown in Table XVI.

TABLE XVI.

	A_0' (acetic).	A_0' (formic).	A_0'' (acetic).	A_0'' (formic).
From Table XV.....	0.0547	0.0459	0.0563	0.0555
Previously given.....	0.0550	0.0455	0.0665	0.0550

II. Discussion of the Nature of the Reaction.—In the study of the catalysis of the cinchona alkaloids in the presence of organic acids, the puzzling question that remains to be answered is that regarding the mechanism of the reaction. That the positive catalyzing influence is not a matter of decreasing concentration of H^+ ion, but is a definite linear function of the concentration of the undissociated acid, has been clearly shown in the preceding pages. This catalytic action has been observed in the case of all such common organic acids as lactic, citric, tartaric, malic, formic, acetic and propionic. What, it must be asked, is the specific role of the organic acid in the mechanism of the reaction? While the data obtained as yet are insufficient fully to answer this question there is one property of an organic acid which leads to a tentative suggestion and that is the readiness with which such an acid yields an acyl amide when heated with ammonia, or a primary or secondary amine. It is conceivable that the tendency to form an acetyl or other acyl derivative of cinchotoxine as an intermediate product is a factor contributing to the conversion of the tertiary cinchona alkaloid into a toxine containing a secondary nitrogen atom. Such an acyl derivative, however, if formed, apparently occurs as an intermediate and not a final product since in all cases examined titration accounted for the total organic acid present.

A reaction favoring the hypothesis advanced is the readiness with which the alkyl halides of the cinchona alkaloids are converted into toxines. Thus, cinchonine methyl iodide on treatment with potassium hydroxide readily yields methylcinchotoxine.¹ Of additional interest in this connection is the influence of the concentration of acetic acid upon the familiar reaction, the conversion of aniline into acetanilide. As shown by Tobias² the amount of acetanilide formed in a given time at constant temperature is dependent upon the concentration of the acetic acid present. A further study of reactions of this type is being continued in this laboratory.

It may be noted finally that any attempt adequately to determine the mechanism of the reaction discussed in this paper must take into consideration all the factors possibly involved. Thus, for example, the mathematical proof given does not necessarily exclude the possibility that partially ionized cinchonine salt, *i. e.*, intermediate ions of the type

¹ Claus and Müller, *Ber.*, 13, 2290 (1880); Miller and Rhoda, *Ibid.*, 27, 1280 (1894); *Ibid.*, 28, 1066 (1895).

² *Ibid.*, 15, 2868 (1882).

Cin. $\frac{\text{HAc}}{\text{H}^+}$, may not take some part in the reaction. Furthermore, as has already been pointed out, from the nature of the case no account has been taken in the calculation of the role played by the totally undissociated alkaloid salt unquestionably present in the solution. In view of the general simultaneous action of ions and undissociated ionogens so ably investigated by Goldschmidt, Acree, Stieglitz and others,¹ a complete mathematical and theoretical interpretation of the reaction must needs, consequently, take into consideration the influence upon the reaction both of the partially and of the completely nonionized alkaloid salt. Such consideration will doubtless largely explain the deviations in reaction rate occasioned by varying initial concentration of the alkaloid. The influence of these and other factors upon the specific reaction rate, both in the case of the cinchona alkaloids and in that of the less involved acetylation of an amine such as aniline, will be made the subject of a subsequent paper.

In conclusion I take this opportunity of expressing my appreciation to Prof. Joel Hillebrand and Dr. L. Q. Adams for a number of helpful suggestions, and my indebtedness to M. J. Gavin for the experimental work in determining the second dissociation constant of cinchonine and of cinchonidine.

Summary.

1. The concentration of H^+ ion in a solution of a cinchona alkaloid containing acids of varying concentration may be calculated with sufficient accuracy to determine the effect of different concentrations of the ion upon the rate of the conversion of the alkaloid into its toxin.

2. The graph obtained by plotting the specific reaction rates against the concentrations of H^+ ion, for solutions of constant concentration with respect to the undissociated organic acid, is a regular curve in which the specific reaction rates change the more rapidly the lower the concentration of the H^+ ion.

3. The specific reaction rate at constant concentration of catalyzing acid in solutions of constant concentration with respect to the alkaloid is directly proportional to the concentration of the univalent cinchonine or cinchonidine ion, *i. e.*, $K_2 \propto (\text{Cin. H}^+)$.

4. The specific reaction rate at constant concentration of the univalent cinchonine or cinchonidine ion is a linear function of the concentration of the undissociated organic acid, *i. e.*, $K_2 = K' + AC'$. This result is particularly significant in that it fully establishes the fact that an undissociated molecule (in this case an un-ionized electrolyte) in homogeneous solution can act as a direct catalytic agent and that through a wide range of concentration (in the case of acetic acid, the law was

¹ *Loc. cit.*

confirmed for concentrations of undissociated acid varying from 0.0485 molal to 7.85 molal).

The relations set forth under 3 and 4 are conveniently expressed in the general equation,

$$K_2 = (K_o' + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

which enables us to extend the application also to varying concentrations of the alkaloid.

5. The specific catalytic action of the three organic acids, formic, acetic and propionic, increases in the order of the acids named. Indeed, the absolute reaction rate for an organic acid, A_o , appears to be directly proportional to the molecular weights of the particular acids concerned—a relationship, however, which is probably accidental.

6. The specific reaction rate, which on theoretical grounds should under like conditions be independent of the initial concentration of the cinchonine or cinchonidine, is found slowly to decrease with increasing concentration of the alkaloid. In view of similar variations in rate of reaction under similar conditions in the case of such catalyses as the inversion of cane sugar and the hydrolysis of esters, these deviations from constancy in the case of the cinchona alkaloids are not to be regarded as abnormal.

7. The specific reaction rates of the two isomeric alkaloids under like conditions bear to each other a constant ratio, whose mean value is, cinchonidine to cinchonine, 1 : 1.21. This difference in rate of conversion is apparently to be attributed solely to the stereoisomeric difference existing between the two alkaloids.

8. A tentative suggestion as to the mechanism of the reaction involved in the conversion of the cinchona alkaloids into their toxins is offered on the basis of the readiness with which organic acids yield acyl derivatives with primary and secondary amines.

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AN APPARATUS FOR THE STUDY OF REACTIONS BETWEEN GASES AND LIQUIDS.

By E. EMMET REID.

Received June 17, 1915.

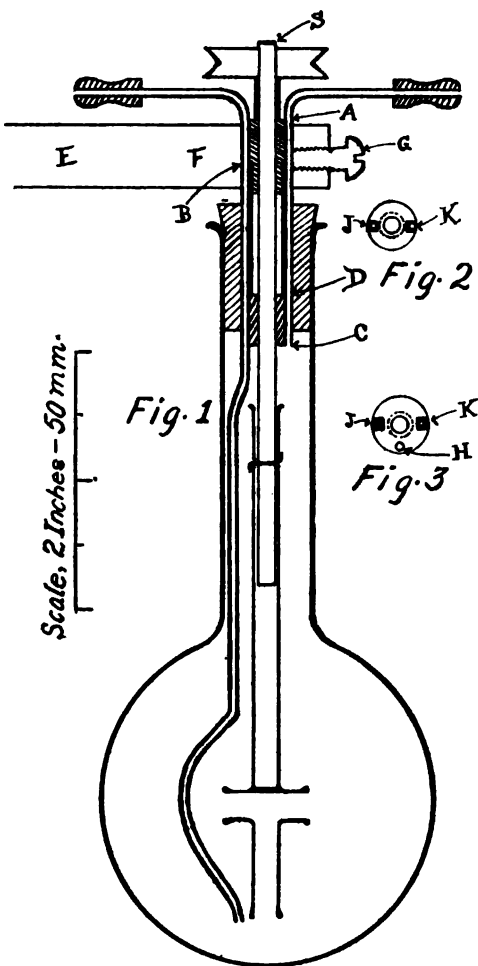
The apparatus here described has been devised and used for the study of catalytic hydrogenation, but may serve for the study of any reaction in which a gas is to be brought into intimate contact with a liquid under constant conditions. The problem is to introduce a high speed stirrer, inlet and outlet tubes, and, possibly, a sampling tube through a comparatively small stopper and to render the whole gas tight for both increased and reduced pressure. The apparatus is shown in the sketch in section, Fig. 1.

The bearing, AC, is made of two pieces of steel rod, AB, and BC, 0.5 and 1.5 inches long, respectively. Both of these have a $\frac{1}{8}$ in. hole drilled longitudinally through them, then the longer one is drilled out to a size of about $\frac{1}{32}$ for most of its length, *i. e.*, from B to D. The shorter piece is turned down for half its length till it fits closely into the other, so that a double bearing is formed, with an enlarged cavity in the central portion. The two parts are assembled and channels about $\frac{1}{16}$ by $\frac{1}{16}$ in. are cut in opposite sides as shown at J and K in cross section in Fig.

Care must be taken that the channels do not cut through the walls of the cavity. The $\frac{1}{16}$ brass tubes that are used for the gas inlet and outlet tubes are laid in these channels which are then filled with solder, the solder more than filling the channels. The excess of solder is turned off in the lathe so that the whole is a perfect cylinder externally and adapted to make a tight joint when passed through a cork.

The stirrer may be of any suitable form, but the Witt centrifugal stirrer shown is one of the best, as, when run at high speed, it effects very thorough mixing. The stirrer may be made of glass and fastened to the shaft by a bit of wire which passes through a hole in the shaft and through holes in the stirrer. The shaft, S, is of $\frac{1}{8}$ in. drill rod and carries a pulley of suitable size. The inlet and outlet tubes are bent as shown and carry enlargements so as to make convenient joints with rubber tubing.

The bearing passes through a hole in a 0.5 in. rod, EF, and is held in place by a set screw, G. This rod is conveniently clamped to a laboratory iron stand.



To assemble the apparatus, the shaft is pushed a short distance into the bearing from the bottom and mercury is poured in. The shaft is then pushed on through, causing the excess of mercury to overflow and leaving the cavity in the bearing filled with mercury. Thus a gastight mercury seal is formed which is tight no matter how fast the shaft rotates. To make a stuffing box gastight would require so much pressure that the rotation of the shaft would be hindered. The mercury seal, though tight, offers no resistance to the motion of the shaft. This seal is tight against either excess or diminished pressure for moderate pressures. The apparatus in use proved to be gastight under a pressure of 3 feet of water. The shaft must fit the bearings very accurately to avoid danger of loss of mercury, but little trouble has been met with in this respect. Lubrication is accomplished by placing a drop of oil above and below the bearings and working the shaft up and down a few times. This should be done each time the apparatus is used.

In case it is desired to take out samples during the course of the reaction, the bearing is cut from somewhat larger rod and a hole is drilled through the assembled bearing, to one side, as shown in section at H in Fig. 3. This hole is stopped by a plug lubricated with oil. For taking out a sample, a piece of 0.25 in. glass tubing is drawn out to a capillary about 6 in. long. This is passed down through the hole in the bearing and the desired amount of liquid drawn out. A hole is drilled in the web of the pulley so that it can be brought over the hole in the bearing and allow the capillary to pass. In studying the velocity of the reaction, the time is taken till the moment that the stirrer is stopped. Taking out a sample requires about one minute. The time for the next period is taken from the moment that the stirrer is again started. Experiments have shown that reactions of this sort, depending on stirring, stand practically still when the stirrer is not in operation.

The size apparatus here described has proved extremely useful for small scale work of a variety of kinds. Obviously, the same plan might be used for apparatus for larger operations. The flask is heated to any desired temperature by being placed in a suitable bath. Temperatures up to 220° have been used. The stirrer has been run by an electric motor, a rubber band serving as a convenient belt. Speeds of 3000 to 4400 revolutions per minute have been obtained without difficulty.

One application of this apparatus will be described in the following communication. It is here described in the hope that it may be of service to those who are working on reactions involving gases and liquids.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN CATALYTIC HYDROGENATION. I. A NEW METHOD OF HYDROGENATION OF VOLATILE SUBSTANCES AND THE RATE OF HYDROGENATION OF ETHYLENE.

BY J. B. RATHER AND E. ERNEST REID.

Received June 17, 1915.

While an enormous amount of work is being done, by a host of investigators, on catalytic hydrogenation, but little of this work has been of a quantitative nature. The present work was undertaken to obtain more information of a quantitative sort on this important reaction. This preliminary paper is intended to put on record some results obtained with a method of hydrogenation somewhat different from those in use, so as to reserve this part of the field for further work.

It has been customary, in hydrogenating volatile substances, to pass a mixture of the gas or vapor and hydrogen over reduced nickel in a long tube. On the other hand, in hydrogenating nonvolatile oils, a common method is to pass hydrogen through the oil containing the catalyst, meanwhile agitating the oil so as to break up the gas bubbles and to keep the catalyst in suspension. The present method is a sort of combination of these two methods in that the volatile substance to be hydrogenated is mixed with hydrogen and this mixture is passed through a nonvolatile inert liquid containing the catalyst, the mixture being thoroughly agitated so as to comminute the gas bubbles and to bring them in intimate contact with the catalyst which is kept in suspension. It is evident that the mixture of hydrogen and reducible gas or vapor may be brought into contact with the nonvolatile oil containing the catalyst in any of the many ways in which hydrogen may be made to act on oils in the various processes that have been proposed for the hydrogenation of fatty acids or their glycerides.

In this preliminary work, ethylene has been the substance studied, though it is intended to extend the work to other gases and to substances sufficiently volatile within the limits of the working temperatures. Ethylene was chosen as it is easy to obtain in pure condition and because its hydrogenation presents the simplest possible case.

The hydrogenation of ethylene has been studied by several, one of the earliest cases of catalytic reduction on record being the work of von Wilde,¹ who exposed a mixture of equal volumes of hydrogen and ethylene to the action of platinum black in an eudiometer and obtained a quantitative yield of ethane. Sabatier and Senderens² passed a similar mixture over reduced nickel and found the union to be complete.

¹ *Ber.*, 7, 353 (1874).² *Compt. rend.*, 124, 1358 (1897).

Experimental.

Preparation of the Catalyst.—One hundred grams of infusorial earth were treated with a solution of 50 g. nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in about 150 cc. water, and the resulting moist mass added to a strong water solution of 60 g. sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, to precipitate the nickel as carbonate. The product was well washed and dried and the nickel carbonate reduced by heating, in a glass tube, just below red heat, in a current of pure dry hydrogen till no more water was formed, and cooled in a current of pure dry carbon dioxide. In order to standardize the catalyst, its activity was tried with cottonseed oil, 70 g. of the oil and 1.0 g. of the catalyst being treated with pure dry hydrogen at 180° in the apparatus described in the preceding communication. The iodine number of the oil was lowered, in 60 minutes treatment, from 113.7 to 44.6. Experiment showed that the catalyst did not deteriorate appreciably during the time that each portion of it was in use.

Temperature.—In all of the experiments, the temperature was maintained at $180^\circ \pm 1^\circ$ by immersing the bulb of the reaction flask in an oil bath, the temperature of which was maintained constant by an oil thermostat with mercury contacts, controlling a gas regulator essentially the same as that previously reported from this laboratory.¹

Materials.—The ethylene was made according to method of Senderens² and washed with sodium hydroxide solution. The hydrogen was from zinc and acid and was washed with alkaline potassium permanganate. As an inert medium, in which to suspend the catalyst, melted paraffin was used.

Procedure.—The gas mixtures were prepared in gasometers, holding about 24 l., which were provided with an arrangement for maintaining nearly constant pressure. The same lot of the mixture was used for the whole series of experiments on any one proportion. Each mixture was analyzed for ethylene by the usual method with fuming sulfuric acid. The mixture of gases was run through concentrated sulfuric to dry it and then into the reaction flask which contained, in each experiment, 1.0 g. of the catalyst and 70 g. of the paraffin. The stirrer was run at 3300 to 3500 r. p. m. In each case, time was allowed for the displacement of air from the apparatus and for the hot paraffin to come to equilibrium with the ethylene, hydrogen and ethane passing through it. The attainment of this equilibrium was shown by constancy in the analysis of successive samples of the issuing gases. The amount of ethane in the product, which is the same as the percentage of reduction of the ethylene, was calculated by the following formula, in which E_1 is the percentage of ethylene in the original mixture and E_2 is the percentage of ethylene in the

¹ *Am. Chem. J.*, 41, 148 (1909).

² *Compt. rend.*, 151, 392 (1911).

products of the reaction. Ethane = $\frac{100E_1 - 100E_2}{100 - E_2}$. Fresh lots of catalyst and of paraffin were used for each 24 l. of mixture.

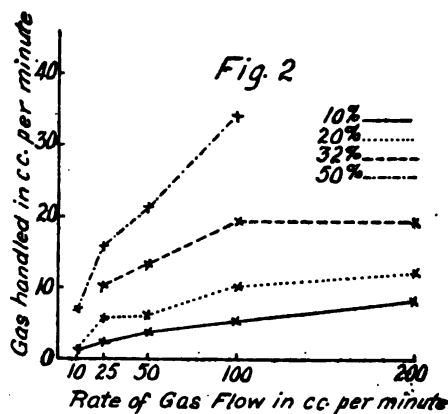
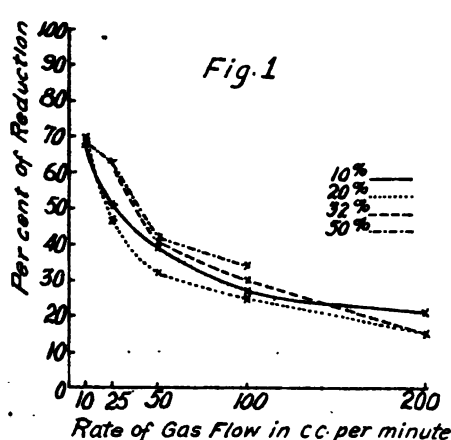
The rate of gas flow and the composition of the original mixture are the only variables studied in the present work. The results are given in tabular form and are reproduced in curves.

RESULTS.

% Ethylene in org. mixture.	Rate of flow cc. per min.	Ethane %.	Reduction %.	Gas handled cc. per min.	% Ethylene in org. mixture.	Rate of flow cc. per min.	Ethane %.	Reduction %.	Gas handled cc. per min.
10.0	10	6.8	68	1.4	32.5	25	20.4	63	10.2
	25	5.1	51	2.5		50	13.4	41	13.4
	50	3.9	39	3.9		100	9.6	30	19.2
	100	2.7	27	5.4		200	4.8	15	19.2
	200	2.1	21	8.4		10	34.1	69	6.8
20.0	10	14.1	70	1.4	49.8	25	31.4	63	15.7
	25	9.4	47	5.9		50	21.1	42	21.1
	50	6.4	32	6.4		100	17.0	34	34.0
	100	5.1	25	10.2					
	200	3.0	15	12.0					

Discussion of Results.

The results are by no means as regular as could be wished, and some are evidently out of relation to the others. They are not to be considered as final. The irregularities may depend on factors not as yet known or controlled. In Fig. 1 the percentage of the ethylene reduced is plotted



against the rate of flow. The interesting result is that, for all of the mixtures, about 70% of the ethylene is reduced when the rate of flow is 10 cc. per minute. All of the results for the 10% mixture are regular and as would be expected. Those for mixtures containing higher percentages of ethylene are by no means so regular and the curves are in

unexpected relations to each other. Doubtless the determining factor is solubility. The reaction is probably taking place between the ethylene and the hydrogen that are dissolved in the paraffin. The mass law then holds for this solution and not for the gases that are not in solution. When the passage of the gas mixture is rapid, the gases are swept through before equilibrium can be established between the gas mixture and the solution.

In Fig. 2 the volume, in cc., of gases made to combine, per minute, is plotted against the rate of flow. As was to be expected, this amount increases with the amount of the gas mixture that is exposed to the action of the catalyst. The results for the different mixtures are in the expected order, those for the rate of 100 cc. per minute being the most instructive. Under these circumstances, in the 50% mixture, 17 cc. of hydrogen is made to combine with 17 cc. of ethylene in 1 minute. Since the 1 g. of the catalyst, as prepared, cannot contain more than 0.1 g. nickel, the volume of this, considered as Ni, would be about 0.01 cc. or less. Hence the catalyst induces the reaction in 3400 times its own volume of the gas mixture in 1 minute. In the experiment with cottonseed oil, given above, the same amount of nickel caused the absorption of 4230 cc. of hydrogen or 423,000 times its own volume of hydrogen in 60 minutes, or 7000 times its own volume in each minute. These volumes are calculated for a temperature of 0° and would be 67% greater at 180°, at which the action really took place. The amount of hydrogen caused to combine with the oil is several times as great as the amount combined with the ethylene, which is as would be anticipated, as the concentration of the ethylene in the paraffin is probably much smaller than the concentration of the olefine in the oil, and the partial pressure of the hydrogen in the mixture is only half so great as in the pure hydrogen. However, the results are of the same order of magnitude.

Further work is anticipated, and it is desired to reserve the study of the various factors influencing the rate of hydrogenation in gaseous mixture as well as the extension of the method to other unsaturated gases and vapors.

Conclusions.

1. It has been shown that hydrogen and ethylene combine readily when a mixture of the two gases is passed through an indifferent oil in which a nickel catalyst is kept in suspension. These experiments indicate a new method of hydrogenating volatile substances.
2. Some quantitative measurements have been made on the rates of combination of ethylene and hydrogen under the influence of a nickel catalyst under different conditions.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

THE TOLYL ESTERS AND TOLUIDIDES OF THE NITROSULFONIC ACIDS OF *p*-XYLENE.

BY RALPH C. HUSTON.

Received July 9, 1915.

In an earlier paper, by Karslake and Huston,¹ three nitrosulfonic acids of *p*-xylene were described. These were prepared by the nitration of *p*-xylenesulfonic acid, or the sulfonation by means of chlorosulfonic acid of nitro-*p*-xylene. Separation of the products was effected by fractional crystallization of the sulfonchlorides from ether and petroleum ether. The configuration was determined by reducing the free acids to the corresponding aminosulfonic acids.

In addition to those described in the previous paper, the following derivatives of the three nitrosulfonic acids of *p*-xylene have been prepared: The *o*-, *m*- and *p*-tolyl esters and the *o*- and *p*-toluidides. A description of these follows.

Preparation of the Tolly Esters.—The crude sulfonchlorides were repeatedly recrystallized until they melted sharply at their respective melting points. The tolyl esters were then prepared as follows:²

0.75 g. of purified cresol (*o*-, *m*-, or *p*-) was mixed in a glass-stoppered bottle with 1 g. of pyridine, 1.75 g. of the purified sulfonchloride was then added. Heat was evolved. The mixture was placed in a constant temperature oven at 90° for fifteen minutes. After standing over night at room temperature, it was washed repeatedly with cold water. The ester was then dissolved in hot alcohol and set aside to crystallize.

Preparation of Toluidides.—The following method was used in the preparation of all of the toluidides:

1.5 g. of the purified sulfonchloride was dissolved in 20 cc. of carbon tetrachloride and treated with an excess (2 cc.) of freshly distilled toluidine (*o*- or *p*-). The solvent was evaporated off on the water bath. The residue was washed repeatedly with 10% hydrochloric acid and dissolved in 5% sodium hydroxide³ solution. After filtering, the toluidide was precipitated with dilute hydrochloric acid, washed and recrystallized, first from 95% alcohol and then from 50% alcohol, until pure.

Derivatives of 6-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolly Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.**—The sulfonchloride dissolved readily in the pyridine-cresol solution, and crystals began to form at once. After washing and recrystallizing four times from alcohol, the ester melted sharply at 66–67° (corr.). It forms nodules of opaque,

¹ THIS JOURNAL, 36, 1244 (1914).

² *Ber.*, 35, 1443 (1902).

³ All the toluidides studied are partially decomposed by 10% sodium hydroxide.

flat, pointed crystals, fairly soluble in alcohol, ether, chloroform, carbon tetrachloride and benzene, only slightly soluble in petroleum ether, and insoluble in water.

Subst.: 0.3566 g.; cc. 0.1 *N* HCl, 10.9. Calc.: N, 4.36%. Found: N, 4.28%.

The Gunning-Jodlbauer modification of the Kjeldahl method was used.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—The sulfonchloride dissolved more slowly in the pyridine-*m*-cresol mixture than it did in the pyridine-*o*-cresol mixture.

The ester is much less soluble in organic solvents than the *o*-tolyl ester and slightly more soluble than the *p*-tolyl ester. It comes down from alcoholic solution in well-formed rhombohedral plates which melt at $71.5-72^\circ$ (corr.).

Subst.: 0.4191 g.; cc. 0.1 *N* HCl, 12.9. Calc.: N, 4.36%. Found: N, 4.31%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—This ester is the least soluble in organic solvents of the tolyl esters of the 6-nitrosulfonic acid. It crystallized from alcohol in clusters of very thin, lustrous plates which melt at $93.5-94.5^\circ$ (corr.).

Subst.: 0.3158 g.; cc. 0.1 *N* HCl, 9.8. Calc.: N, 4.36%. Found: N, 4.35%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound comes down from ninety-five per cent. alcohol in colorless plates and from fifty per cent. alcohol in clusters of very fine, flat needles. It is readily soluble in alcohol, chloroform, carbon tetrachloride, and benzene, less soluble in ether and petroleum ether; but insoluble in water. M. p. $126.5-127.5^\circ$ (corr.).

Subst.: 0.2587 g.; cc. 0.1 *N* HCl, 15.9. Calc.: N, 8.75%. Found: N, 8.61%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This is less soluble in organic solvents than the *o*-toluidide of the same acid. It began to precipitate immediately from the reacting mixture. It comes down from fifty per cent. alcohol in clusters of long, silky, colorless filaments. M. p. $135-136^\circ$ (corr.).

Subst.: 0.2807 g., 0.3476 g.; cc. 0.1 *N* HCl, 17.1, 21.5.

Calc.: N, 8.75%. Found: N, 8.53%, 8.68%.

Derivatives of 3-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—The sulfonchloride dissolved more slowly in the pyridine-*o*-cresol mixture than did either of its isomers. The mixture darkened when heated to 90° , but solidified immediately on cooling. This is the least soluble in organic solvents of the tolyl esters of the 3-nitrosulfonic acid. It crystallizes from alcohol in hard, opaque prisms which melt sharply at $151.5-152^\circ$ (corr.).

Subst.: 0.3743 g.; cc. 0.1 *N* HCl, 11.55. Calc.: N, 4.36%. Found: N, 4.29%.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—The sulfonchloride dissolved a little more rapidly in the pyridine-*m*-cresol mixture than in the pyridine-*o*-cresol mixture. The ester comes down from alcohol in lustrous,

colorless plates. It is slightly more soluble than the *o*-tolyl ester of the same acid. M. p. 107.5–108° (corr.).

Subst.: 0.2989 g.; cc. 0.1 *N* HCl, 9.1. Calc.: N, 4.36%. Found: N, 4.27%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—The sulfonchloride dissolved readily. The reacting mixture did not completely solidify on standing over night. It was washed repeatedly with cold water until it solidified. This ester is much more soluble in organic solvents than the other tolyl esters of the same acid. On evaporation of its alcoholic solution at room temperature it tended to form an oily deposit. Crystallization is best carried on at about 10°. It comes down in fine, poorly formed, needle-like plates which melt after ten recrystallizations at 76–77° (corr.).

Subst.: 0.3128 g.; cc. 0.1 *N* HCl, 9.6. Calc.: N, 4.36%. Found: N, 4.3%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound is slightly more soluble in organic solvents than the *p*-toluidide of the same acid. It comes down from 50% alcohol in fine, lustrous, rhombohedral plates. M. p. 143.5–145° (corr.).

Subst.: 0.2638 g.; cc. 0.1 *N* HCl, 16.3. Calc.: N, 8.75%. Found: N, 8.65%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—A heavy precipitate was formed immediately on the addition of the *p*-toluidine to the solution of sulfonchloride. The toluidide has about the same solubility in organic solvents as the *o*-toluidide of the 6-nitro acid. Crystallized from fifty per cent. alcohol it forms long, flat, lustrous needles which melt sharply at 158.5–159° (corr.).

Subst.: 0.2611 g., 0.2125 g.; cc. 0.1 *N* HCl, 16.1, 13.1.

Calc.: N, 8.75%. Found: N, 8.63%, 8.64%.

Derivatives of 5-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—This ester is much less soluble in organic solvents than the *o*-tolyl ester of the 6-nitro acid, and of about the same solubility as the *o*-tolyl ester of the 3-nitro acid. It crystallizes from alcohol in long (4 cm.), flat, opaque, soft needles which have a constant melting point of 99–100° (corr.).

Subst.: 0.3676 g.; cc. 0.1 *N* HCl, 11.3. Calc.: N, 4.36%. Found: N, 4.31%.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—This is less soluble than the *o*-tolyl ester of the same acid and but slightly more soluble than the *p*-tolyl ester. It forms clusters of fine, flat, lustrous, brittle needles. M. p. 110–111° (corr.).

Subst.: 0.3179 g.; cc. 0.1 *N* HCl, 10.0. Calc.: N, 4.36%. Found: N, 4.40%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_2C_6H_4CH_3$.—This is the least soluble in organic solvents of any of the tolyl esters. It crystallizes from alcohol in long (5 cm.), lustrous, needle-like plates which melt at 117.5–118.5° (corr.).

Subst.: 0.3214 g.; cc. 0.1 *N* HCl, 10.2. Calc.: N, 4.36%. Found: N, 4.42%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound crystallizes from fifty per cent. alcohol in lustrous plates which retain a slight yellow color after repeated recrystallization. It is a little more soluble in organic solvents than the *p*-toluidide of the same acid. M. p. 140.5–141° (corr.).

Subst.: 0.2855 g., 0.2681 g.; cc. 0.1 *N* HCl, 17, 16.6.

Calc.: N, 8.75%. Found: N, 8.34%, 8.67%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—It is the least soluble in organic solvents of the toluidides studied. It crystallizes in lustrous elongated plates which melt at 143.5–144.5° (corr.).

Subst.: 0.2783 g.; cc. 0.1 *N* HCl, 17.1. Calc.: N, 8.75%. Found: N, 8.61%.

Summary and Discussion.

A comparison of the melting points of tolyl esters of the nitrosulfonic acids of *p*-xylene reveals some peculiarities which are worthy of note in the light of existing theories. The tolyl esters of the 5-nitro and 3-nitro acids follow the rule of symmetry, *i. e.*, the melting points increase from ortho to meta to para. The melting points of the tolyl esters of 4-nitro acid, on the other hand, decrease from ortho to meta to para. This is especially peculiar in the light of a theory advanced by Smiles,¹ which assigns the lowering of fusion point to intramolecular collision. An examination of the structural formula of the *o*-tolyl ester of the 3-nitro acid shows that the substituting groups are in the most compact arrangement possible, while the melting point is higher than that of any of the other tolyl esters studied, *i. e.*, 151°. No record of esters of similar structure could be found in the literature.

The toluidides are more regular as regards their melting points. The *p*-toluidide of each acid melts at a higher temperature than the *o*-toluidide.

For any given acid the solubility of its derivatives in organic solvents decreases as the melting point increases.

As a rule the derivatives of the 5-nitro acid are less soluble than the derivatives of its isomers.

EAST LANSING, MICH.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF DIPHENYLUREACHLORIDE ON ORGANIC BASES.

BY WILLIAM M. DEHN AND EARL M. PLATT.

Received June 28, 1915.

Michler² first prepared diphenylureachloride by treating diphenylamine with phosgene in chloroform solution. Its action on ammonia

¹ "Relation between Chemical Constitution and Some Physical Properties," p. 208.

² *Ber.*, 8, 1665 (1875); 9, 396 (1876); see also Girard and Wilm, *Bull. soc. chim.*, 25, 251 (1901); Erdmann and Herth, *J. prakt. Chem.*, [2] 56, 6 (1897); melts at 189°.

was found by him to yield α,α -diphenylurea at 100° , but diphenylamine, ammonia and carbon dioxide at 150° . Its action on hydrazine hydrate was studied by Toschi¹ who obtained diphenylsemicarbazide and tetraphenylhydrazodicarboxamide. Its action on diethylamine yielded diethyldiphenylurea;² on aniline in chloroform solution, triphenylurea;³ on nitraniline⁴ at 120° , *m*-nitrotriphenylurea and *p*-nitrotriphenylurea; on ethylaniline, ethyltriphenylurea;⁵ on diphenylamine, tetraphenylurea⁶—this by nitration⁷ yielded hexa- and octanitrotetraphenylurea. Other studies of the action of diphenylureachloride on organic bases have not been made.

The following studies were undertaken not only to extend our knowledge of its reactions but also to determine whether this complex halogen derivative and organic bases react in anhydrous ether solutions like previously⁸ investigated halogen compounds.

While the mechanism of reaction was found to be the same as with acetyl chloride,⁹ benzoyl chloride¹⁰ and other halides, four points of exceptional interest were developed. First, the reactions were found to be sluggish except with piperidine, *p*-toluidine, and some of the lower fatty amines. Second, few additive compounds were obtained. Third, other examples of the noninterchangeability¹¹ of parts of the pentavalent nitrogen compounds were observed. Fourth, a remarkable example of "steric hindrance" was observed with the toluidines.

That diphenylureachloride is less reactive than alkyl or acyl halides toward bases, is to be expected. However, that it is immediately reactive with piperidine and some of the lower fatty amines, but absolutely nonreactive, except at elevated temperatures, with other bases such as toluidine, etc., is irreconcilable with the usual conceptions of the ionic theory.¹² Moreover—since the reactions, here as before, were promoted

¹ *Gazz. chim. ital.*, 44, I, 443 (1914). Melts at 154° and 215° , respectively.

² Michler, *Ber.*, 9, 711 (1875). Melts at 54° .

³ Michler, *Ber.*, 9, 398, 715 (1875); Gebhardt, *Ber.*, 17, 2093 (1884); Steindorff, *Ber.*, 37, 963 (1894); Reudler, *Rec. trav. chim.*, 33, 35 (1914). Melts at 136° .

⁴ Tellmann and Bonhöffer, *Ber.*, 20, 2121 (1887). These melt at 155° and 176° , respectively.

⁵ Michler, *Ber.*, 9, 712 (1875); Kaufmann, *Ber.*, 14, 2185 (1881). Melts at 80° .

⁶ Michler, *Ber.*, 9, 710 (1875); 12, 1166 (1879); Strohmman, *J. prakt. Chem.*, [2] 264 (1897). Melts at 183° .

⁷ Reudler, *Rec. trav. chim.*, 33, 35 (1914).

⁸ THIS JOURNAL, 33, 1588, 1598 (1911); 34, 286, 290, 1399, 1409 (1912); 36, 2091 (1914).

⁹ *Ibid.*, 34, 1409 (1912).

¹⁰ *Ibid.*, 36, 2091 (1914).

¹¹ *Ibid.*, 36, 2095 (1914).

¹² Evidences of certain nonionic organic reactions, as well as a more rational explanation of such reactions were previously given. *Am. Chem. J.*, 40, 91-97 (1908); THIS JOURNAL, 31, 1220-22 (1909); 33, 1589-92 (1911); 34, 287, 291, 1400-2, 1410-11 (1912); 36, 2093-96 (1914).

by sunlight or by heat, and gave rise to additive products or dissociated molecules of such additive products—little dependence can be placed in the ionic theory to account for the mechanism of this type of reaction. However, the best evidence obtained to cast doubt on an ionic explanation of these reactions was found in the noninterchangeability¹ of parts of the additive, pentavalent-nitrogen compound. This phenomenon is illustrated by equations:



That is, *diphenylureachloride* easily adds one molecule of *piperidine* to form *diphenylpiperidylurea hydrochloride*, but this additive compound could not be formed by the addition of *hydrogenchloride* to *diphenylpiperidylurea*.

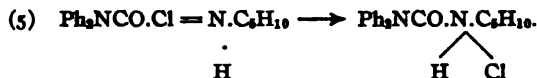
An ionic explanation of the first reaction may be indicated in the equation:



but, in the second reaction, similar ionic dissociation would be necessary, at least an ionic dissociation of hydrogen chloride² must be assumed:



Now since this last reaction in aqueous solutions is real and known, reaction (2) may be expected to yield the same product as in reaction (1) but, as a matter of fact, such product is not obtained, hence it may be concluded: (a) an ionic dissociation of hydrogen chloride does not take place in anhydrous ether solution and (b) an ionic explanation of the anomalous phenomena of Equations, 1 and 2 is untenable. A more satisfactory explanation is expressed in the equation:



As enunciated before, the possibility of reaction in such cases is conditioned both by a tendency to coalesce and by a tendency to undergo molecular rearrangement.

In the first place, the tendency to coalesce by means of residual of partial valencies³ involves different affinity constants of the reacting

¹ This same noninterchangeability was previously observed with benzoyl chloride compounds. *THIS JOURNAL*, 36, 2095 (1914).

² For a discussion and the literature of nonionic dissociation of hydrogen chloride see Mellor's "Statics and Dynamics," p. 290. Since neither the solvent nor sunlight promotes reaction (2) above, Baly's contention that these alone are the "openers of chemical reactivity" cannot hold, see *THIS JOURNAL*, 37, 986 (1915).

³ This assumption of preliminary molecular coalescence gathers support from consideration of the fact that only such *unsaturated* compounds react. See Nef, *Ann.*, 298, 202 (1898). It may be observed that application of the methylene theory of dissociation is entirely inapplicable to these reactions.

compounds, hence, as actually found, different speeds of reaction or complete inhibition of reaction are met with. Such varied systems of molecular aggregation may tend to undergo simple reversible reaction or a non-reversible molecular rearrangement. Thus, while the following may be formed:



it is conceivable that the hydrogen atom is held by the chlorine atom so tenaciously¹ that molecular rearrangement is impossible.

Since energy is required to promote molecular rearrangements, it may be assumed that, owing to varied affinity constants, in different cases, more or less resistance or inertia will be met with before yielding the non-reversible, pentavalent-nitrogen, molecular compound. Now, as a matter of fact, such resistance or inertia is met with, for light or heat energy is required to start and advance certain reactions. For instance, some of the reactions take place at room temperature without applying direct sunlight; some are resistant to direct sunlight but may be promoted by moderate heat; finally, others are promoted only by extreme heat. Whatever may be the cause of these varied resistences in different cases, it must be observed that the ionic theory is helpless to account for the progress of the reaction.

A Case of "Steric Hindrance."

The toluidines showed different speeds of reaction with diphenylurea-chloride. When equimolecular quantities in equal ether volumes were prepared, the *p*-toluidine gave a rapid precipitation of wart-like masses of needles. The *m*-toluidine yielded a small quantity of ball-like masses which was slowly added to during 4 months' standing in sunlight. The *o*-toluidine yielded, after 5 months' standing in sunlight, mere traces of microscopical prismatic needles.

When heated on the water bath or in sealed tubes, ether solutions of diphenylureachloride and each of the toluidines yielded in a few hours the respective tolyldiphenylurea. The formation of such tolyldiphenylurea was easily observed to be most rapid with *p*-toluidine and least rapid with the *o*-toluidine. In other words, *p*-toluidine yields the tolyldiphenylurea by application of light or of heat. The *m*-toluidine yields the tolyldiphenylurea, slowly by application of light, but rapidly by application of heat. The *o*-toluidine yields the tolyldiphenylurea only by application of heat.

What is the cause of these resistences to the advance of the reactions, particularly in the case of *o*-toluidine? Of course, in the case of *o*-toluidine

¹ It must be remembered that hydrogen chloride is not decomposed below 1000° by heat alone.

Victor Meyer's steric hindrance or retardation hypothesis¹ suggests itself; however, since the validity of this hypothesis has been questioned and disproven by Baly and Stewart,² Rosanoff and Prager,³ and others, some other hypothesis must be sought, to explain the effects of heat and light on these reacting mixtures. Baly and Stewart⁴ advance a hypothesis of "nascent carbonyl group," to account for differences of speed of reaction observed with various ketones. However, such a hypothesis is inapplicable to these reactions of diphenylureachloride since no "pseudonascent" hydrogen atom exists in the reacting substances, since the carbonyl group probably is unimportant in these reactions⁵ and since no such tautomerism is involved.

However, if we assume in cases of *p*- and *o*-toluidines the following initial additions:



it is conceivable that the two complexes, while not necessarily possessing different steric hindrances, may possess different tendencies to rearrange. The centers of gravity of the two toluidine molecules being differently located may possibly influence the nitrogen affinities so that the nitrogen atom of *o*-toluidine does not exert sufficient attraction on the CONPh_2 group to bring about a molecular rearrangement.

This interesting phenomenon will be studied anew, especially by way of comparison of the effects of the toluidines on the following types of halogen derivatives:



Method of Study.

The anhydrous ether solutions of diphenylureachloride were treated with the respective anhydrous bases in equimolecular quantities. Bottles containing these mixtures were tightly corked and set aside for observation. Provided water was rigorously excluded and sufficient ether to dissolve the materials was used, the formation of a precipitate indicated either the additive compound, the hydrochloride of the original base, or a mixture of the two. Such precipitates always indicated a reaction, hence speeds of reaction could roughly be estimated by mere observation of the quantities of the precipitate. In some cases the ether solu-

¹ *Ber.*, 27, 510, 1580, 3146 (1894); 28, 1254 (1895); 29, 836 (1896); Kellas, *Z. physik. Chem.*, 24, 221 (1897); Eckstand, *J. prakt. Chem.*, 38, 267 (1888).

² *J. Chem. Soc.*, 89, 489, 502, 514, 618 (1906).

³ *THIS JOURNAL*, 30, 1895, 1908 (1908).

⁴ *J. Chem. Soc.*, 89, 491 (1906).

⁵ Compare the action of alkyl halides on toluidines.

tions were heated in sealed tubes or under return condensers to promote reactions.

The precipitates were filtered off, washed with anhydrous ether and dried in desiccators. They were then either analyzed for chlorine to determine the general composition of the mixture, or were treated with water to hydrolyse and to dissolve the hydrochlorides. The aqueous solutions were extracted with ether, dried with calcium chloride, and concentrated. In this manner, the Ph_2NCO -substituted products of the bases were obtained pure.

The original ether solutions were shaken with dilute hydrochloric acid to remove unchanged bases; the ether extracts were dried with calcium chloride and concentrated. In this manner, mixtures of unchanged diphenylureachloride and the Ph_2NCO -substituted derivatives of the bases were obtained. When the former was nearly quantitatively transformed by the original reaction, or when the latter was difficultly soluble in ether, separations were easy. In cases of lower aliphatic bases, however, oily residues were obtained; these could not be made to yield pure Ph_2NCO -substituted products.

Primary Amines.

***p*-Toluidine.**—Diphenylureachloride in anhydrous ether was treated with a slight excess of *p*-toluidine and heated in a sealed tube at 70° for four hours. A mass of crystals formed. The mixture was treated with dilute hydrochloric acid so as to separate the unchanged toluidine; more ether was added and the mixture was thoroughly shaken. The ether solution was separated, dried with calcium chloride and concentrated, when transparent prismatic needles melting at 130° were obtained.

Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{NH}\cdot\text{CON}(\text{C}_6\text{H}_5)_2$: N, 9.27%. Found. N, 9.47%.

p-Tolyldiphenylurea is very soluble in chloroform and ether, less soluble in alcohol and benzene and insoluble in water.

When 1 g. of diphenylureachloride and 0.4 g. of *p*-toluidine were brought together in anhydrous ether solutions, such solutions remained clear at first, then clouded, and during four months in direct sunlight, precipitated 0.2 g. of wart-like masses of needles. These were separated and were found to melt above 200° , to dissolve rapidly in water with a spinning motion.¹

Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2\cdot(\text{C}_6\text{H}_5)_2\text{NCOCl}$: Cl, 10.47%.

Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$: Cl, 24.70%. Found: 17.45.

Evidently about 50% of the crystalline mixture was *p*-tolyldiphenylurea hydrochloride.

***m*-Toluidine.**—The equimolecular mixture was heated at 115° for four hours. Crystals melting at 130 – 180° were obtained. After treating

¹ THIS JOURNAL, 34, 1400 (1912); 36, 2093 (1914).

with dilute hydrochloric acid and extracting with ether, as with *p*-toluidine, transparent prismatic needles, melting at 125–126° were obtained.

Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{NHCON}(\text{C}_6\text{H}_5)_2$: N, 9.27%. Found: N, 9.16 and 9.51%.

m-Tolylidiphenylurea crystallizes from alcohol in transparent rhombic plates.

When 1 g. of diphenylureachloride and 0.4 g. of *m*-toluidine were brought together in ether solution, 0.2 g. of precipitate was formed after standing in four months' sunlight. The precipitate consisted of brown-red balls and gave the spinning motion on water.

o-Toluidine.—After heating the reacting mixture in a sealed tube at 115° for four hours, a crystalline mass, melting at 121–126°, was obtained. After purifying, rectangular plates and tufts of needles melting at 119° were obtained. Since they contained 9.35% of nitrogen, pure *o*-tolylidiphenylurea was obtained.

An ether solution of the reacting substances, exposed to four months' sunlight, yielded only 1 mg. of brown ball-like masses.

Phenylhydrazine.—Equimolecular quantities of diphenylureachloride and phenylhydrazine in anhydrous ether solution were heated under a return condenser for two hours. A crystalline mass, increasing on standing, was formed. These crystals, incompletely soluble in water and containing merely traces of chlorine, after treatment with water and recrystallization from absolute alcohol, gave rhombic plates which melted at 149–150°.

Calc. for $\text{C}_6\text{H}_5\text{NHNHCON}(\text{C}_6\text{H}_5)_2$: N, 13.86%. Found: N, 13.92%.

That this is *i*,*4*,*4*-triphenylsemicarbazide is concluded from a comparison of melting points. Rape and Labhardt¹ prepared 2,4,4-triphenylsemicarbazide, melting at 128°. H. Richter² prepared 1,1,4-triphenylsemicarbazide, needles melting at 193°. Therefore the indicated structure is the most probable.

When 1 g. of diphenylureachloride and 0.47 g. of phenylhydrazine were permitted to stand in anhydrous ether in sunlight for two months, 0.45 g. of a crystalline mass, melting³ at 227° and containing 7.15% of chlorine, was obtained.

Calc. for $\text{C}_6\text{H}_5\text{N}_2\text{H}_3\cdot\text{HCl}$: Cl, 24.33%.

Calc. for $(\text{C}_6\text{H}_5\text{N}_2\text{H}_3)_2\text{HCl}$: Cl, 14.03%.

Calc. for $\text{C}_6\text{H}_5\text{N}_2\text{H}_3\cdot(\text{C}_6\text{H}_5)_2\text{NCOCl}$: Cl, 10.14%.

That the mixture contained 1,4,4-triphenylsemicarbazide or its *hydrochloride* is evident.

¹ *Ber.*, 33, 247 (1900).

² Dissertation.

³ Phenylhydrazine forms two hydrochlorides: $\text{C}_6\text{H}_5\text{N}_2\text{H}_3\cdot\text{HCl}$, melting at 240° (Broche, *J. prakt. Chem.*, [2] 50, 114 (1894)) or at 243–246° (Autenrieth, *Ber.*, 29, 1656 (1896)); $(\text{C}_6\text{H}_5\text{N}_2\text{H}_3)_2\text{HCl}$, melting at 225° (Allain le Canu, *Compt. rend.*, 129, 105 (1899)); (Schmitz and Dumont, *Chem. Zig.*, 21, 511).

p-Tolyldiazine.—Only a little precipitate was formed in two months.

Diphenylhydrazine (asym.).—Similar results.

Benzylphenylhydrazine (asym.).—After heating for 20 hours under return condenser, a considerable quantity of transparent crystals was obtained.

α -Naphthylamine.—A heavy precipitate containing a dye was obtained in direct sunlight.

Benzidine.—Sheaves of needles.

p-Aminophenol.—Heating for 4 hours at 200° yielded a blue-black dye.

o-Chloroaniline.—In sunlight for two months, a little gray precipitate was obtained; heated for 4 hours at 200°, a dark-brown solid was obtained.

p-Bromoaniline.—Two months' direct sunlight gave a quantity of wedge-shaped crystals.

p-Anisidine.—Heating for 4 hours at 200° yielded a deep-red, gummy oil.

Isobutylamine.—Sheaves of needles; a refractory oil.

Hexylamine.—Crystals softening at 183° and melting at 230°; original ether solution yielded a refractory oil.

Heptylamine.—A refractory oil.

Secondary Amines.

Piperidine.—A voluminous precipitate was formed at once. The crystals melted at 213°, and were soluble in water.

Calc. for $(C_6H_5)_2NCOCl.NC_4H_9$: Cl, 11.19%.

Calc. for $NC_4H_9.HCl$: Cl, 29.17%. Found: Cl, 15.70.

Therefore the crystals contained 75% of *diphenylpiperidylureahydrochloride*. Its presence was further indicated by spinning motions produced when the crystals were floated on water. After treating with water, etc., hexagonal and rhomboidal plates melting at 122° were obtained.

Calc. for $(C_6H_5)_2NCO.NC_4H_9$: C, 77.09%; H, 7.19%. Found: C, 77.17%; H, 7.31%.

Evidently *triphenylpiperidylurea* (*triphenylcyclopentamethylensurea*) was formed. A toluene solution of this compound treated with a toluene solution of hydrogen chloride failed to yield any precipitate (of the hydrochloride) even though standing for five months in sunlight.

Diisobutylamine.—Rhombic plates melting at 240°; ether solution yielded hyroscopic needles melting at 60°.

Diisooctylamine.—Crystals melting at 147–230°; refractory oil.

Diphenylamine.—Amorphous precipitate.

Phthalimide.—Heating for two hours at 220° in xylene solution gave no evidence of a reaction.

Tertiary Bases.

Quinoline.—A quantity of amorphous precipitate.

Pyridine.—A red-black precipitate.

Picoline.—A chocolate-colored precipitate.

Triethylamine.—Transparent prismatic needles.

Triisobutylamine.—Cubes and spindle-shaped crystals.

Triisoamylamine.—Minute needles.

Diethylaniline.—A small amount of dirty brown precipitate.

Tribenzylamine.—Cubic masses and boat-shaped prisms.

Some of these compounds will be further investigated.

Summary.

1. Diphenylureachloride reacts sluggishly with most bases; such reactions are promoted by sunlight or by heat.
2. Additive products are first formed; these yield by action of heat, water, etc., the Ph_2NCO -substituted products of the base.
3. Evidences for the nonionic nature of these reactions are given.

SEATTLE, WASHINGTON.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE COMPARATIVE BEHAVIOR OF THIOUREA AND UREA TOWARDS ACETIC ANHYDRIDE.

By EDWARD F. KOHMANN.

Received July 5, 1915.

During the course of work in this laboratory, Professor Treat B. Johnson asked the author to determine whether there would be any formation of hydantoin if thiourea were used instead of ammonium thiocyanate in the reaction described by Johnson and Nicolet¹ for the preparation of 2-thio-3-benzoyl hydantoin.² Exactly the same conditions were employed, as well as the same reagents in the same proportions, as described for the preparation of the hydantoin, with the exception that the ammonium thiocyanate was replaced by an equivalent quantity of thiourea. Although no trace of a thiohydantoin was detected, a small amount of a substance was obtained which could be crystallized from water or alcohol in the form of colorless slender prisms. As this substance had a melting point of 165° it was concluded that it must be acetyl thiourea. In order to definitely establish this point it was decided to prepare acetyl thiourea for comparison and the method of Nenki³ with slight modifications, was adopted.

Nenki assigned to this derivative a melting point of 111.5° which he

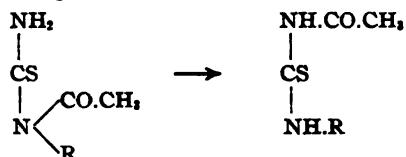
¹ THIS JOURNAL, 33, 973 (1911); *Am. Chem. J.*, 49, 202 (1913).

² A discussion of this reaction and its application with anhydrides other than acetic will follow in a future paper by Bernard H. Bailey.

³ *Ber.*, 6, 599 (1873).

later¹ corrected to 165°. He stated that when thiourea was gently warmed with acetic anhydride it readily went into solution. On cooling, the solution solidified to a yellow crystalline mass which, after repeated crystallizations from water, finally yielded colorless prisms of acetyl thiourea.

Werner² found that when symmetrical diaryl thioureas were heated with acetic anhydride they yielded acetanilides and the corresponding mustard oils, whereas symmetrical dialkyl thioureas yielded the corresponding monoacetyl derivatives. Hagershoff³ later made the observation that if the reaction mixture was heated to only 80° the expected monoacetyl derivative was obtained in all cases. From the monosubstituted thioureas, Hagershoff obtained in each case a labile and a stable monoacetyl modification. When the former was heated slightly above its melting point it soon solidified and rearranged into the latter modification. Wheeler⁴ has shown that a molecular rearrangement of the following type takes place in this change:



It is interesting to note that in no case has a diacetyl derivative been obtained. Diacetyl urea has been prepared by several methods but not by the direct interaction of urea with acetic anhydride, whereas diacetyl thiourea is not known. Symmetrical dibenzoyl urea is also well known, whereas dibenzoyl thiourea has not been synthesized. It has now been found that thiourea forms a diacetyl derivative when heated with acetic anhydride although urea, under the same conditions, forms only the monoacetyl derivative. Curiously enough, diacetyl thiourea has a bright lemon-yellow color whereas monoacetyl thiourea is colorless.

In an attempt to prepare acetyl thiourea, pure reagents were used. Nevertheless, as was observed by Nenki, a yellow product resulted. This color was not changed by one crystallization from either water, alcohol or glacial acetic acid. As it seemed unreasonable that this color should be due to anything but the presence of a definite compound and as the product had a melting point of 150–155° instead of 165°, an analysis was made and the nitrogen content found to be 19.5%. This was evidence that the product was a mixture of mono- and diacetyl thioureas. As will be seen in the experimental part of this paper such a conclusion was correct and by crystallizing from acetic anhydride diacetyl thiourea

¹ Ber., 6, 905 (1873).

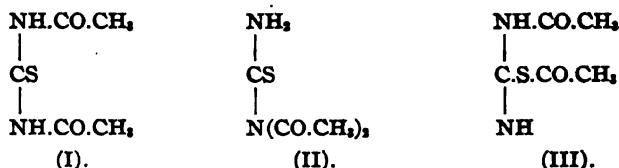
² J. Chem. Soc., 59, 396 (1891).

³ Ber., 32, 3649 (1899).

⁴ Am. Chem. J., 27, 270 (1902).

could be obtained. Under these conditions urea yielded only a monoacetyl derivative.

Diacetyl thiourea may be represented by any one of the following structural formulae, or even by the corresponding pseudo forms of (I) and (II):



From analogy, according to Wheeler, (II), and according to Dixon and Hawthorn,¹ (III) should undergo molecular rearrangement, on being heated to their melting points, to yield (I). Diacetyl thiourea, however, when heated to the melting point, is apparently unchanged. If heated for some time at a somewhat higher temperature it assumes a darker color and undergoes a slow decomposition with the evolution of gas bubbles. On cooling, the viscous liquid is rather slow to solidify. Richter² states that monoacetyl thiourea may be obtained from thiourea and acetic anhydride or from cyanamide and thioacetic acid. The latter synthesis he states, argues in favor of a pseudo structure. But it is conceivable that a molecular rearrangement might easily take place under the conditions of this reaction and the normal derivative result. Hence Formula I seems the most reasonable to assign to diacetyl thiourea.

Experimental Part.

Preliminary Experiment.—One and eight-tenths grams of thiourea were dissolved in 5 cc. of acetic anhydride by heating to boiling. The solution was yellow and the reaction was probably complete within a short time, but the heating was continued for one hour at 100° in a water bath. On cooling, yellow prisms separated. These crystallized from water, alcohol, or glacial acetic acid and melted at about 150–155°. The portion crystallized from glacial acetic acid was dried at 100° for analysis.

Calc. for $\text{C}_4\text{H}_6\text{ON}_2\text{S}$: N, 23.7; for $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{S}$: N, 17.5. Found: 19.5.

Monoacetyl Thiourea.—One-half gram of the above product was dissolved in 10 cc. of boiling water and the solution heated for one hour at 100° in a water bath. On cooling, colorless prisms separated which melted at 165° to a clear colorless liquid.

Calc. for $\text{C}_4\text{H}_6\text{ON}_2\text{S}$: N, 23.7. Found: 23.5.

Diacetyl Thiourea.—One-half gram of the yellow product described above was dissolved in about 5 cc. of hot acetic anhydride and heated at 100° in a water bath for one hour. On cooling, clusters of transparent

¹ *J. Chem. Soc.*, 91, 122 (1907).

² *Organische Chemie*, 1, 501 (1909).

pale yellow blade-like prisms separated which melted at 151–152° to a transparent yellow oil. These were dried in a current of air until free from the odor of acetic anhydride. They could then be heated to 110° without any loss of weight but meanwhile assumed a bright lemon yellow color. Nitrogen determination:

Calc. for $C_4H_5O_2N_2S$: N, 17.5. Found: 17.4. The analysis of a later preparation gave 17.6% and 17.5%.

If diacetyl thiourea is crystallized from a concentrated solution in acetic anhydride it separates in the form of a bright lemon-yellow product. If allowed to crystallize slowly from a dilute solution larger crystals are obtained which are pale yellow and transparent. On heating to 100° they assume a bright lemon-yellow color, losing nothing in weight and retaining their original form.

Monoacetyl Urea.—One gram of urea was dissolved in 10 cc. of acetic anhydride by boiling and the heating continued for one hour at 100°. On cooling, clusters of colorless prisms separated, melting at 212°. These were dried at 110° with no loss in weight.

Calc. for $C_4H_5O_2N_2$: N, 27.4. Found: 27.3.

URBANA, ILL.

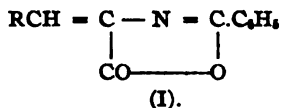
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXIII. THE CONDENSATION OF CINNAMIC ALDEHYDE WITH HYDANTOINS.¹

By TREAT B. JOHNSON AND RICHARD WRENSHALL.

Received June 28, 1915.

Erlenmeyer's method of synthesizing α -amino acids, the first step of which involves the condensation of hippuric acid with an aldehyde giving an azlactone (I), has found a wide application for the preparation of amino



acids containing aromatic groups. The majority of the aromatic aldehydes which have been studied, have been shown to condense smoothly with hippuric acid giving good yields of the corresponding azlactones. Attempts to synthesize aliphatic α -amino acids by application of Erlenmeyer's method with aliphatic aldehydes have been attended with very little success. Erlenmeyer and Kunlin² were the first to apply the method with an aliphatic aldehyde with the object of developing a new synthesis of leucine (V). They condensed isobutylaldehyde with hippuric acid

¹ Part of a dissertation presented by Mr. Richard Wrenshall to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

² *Ann.*, 316, 145 (1901).

Wheeler and Brautlecht¹ were the first to show that cinnamic aldehyde will condense with hydantoins by preparing 1-phenyl-2-thio-4-cinnamalhydantoin from 1-phenyl-2-thiohydantoin by interaction with cinnamic aldehyde. The yield of their condensation product was recorded as being equivalent to 93.6% of the theoretical. We now find that plain hydantoin and also 2-thiohydantoin condense with this aldehyde forming the corresponding 4-cinnamalhydantoin (XIII), and 4-cinnamalthiohydantoin (XXI), respectively. The yields in both cases were good. Theoretically, these two unsaturated hydantoins as well as Erlenmeyer's and Matter's² azlactone (VII), should be capable of existing in more than one modification. In fact, in the case of the azlactone (VII), Erlenmeyer and Matter state that they encountered difficulties in its purification and actually assumed that they were probably dealing with stereoisomeric forms which were inseparable. We examined very carefully both of our condensation products, in hopes of detecting here stereoisomers,³ but no evidence was found that would point to the conclusion that either substance existed in more than one form.

2-Thio-4-cinnamalhydantoin (XXI), was desulfurized smoothly by vigorous treatment with chloroacetic acid, giving the hydantoin (XIII). Therefore, for the synthesis of the amino acid (XV) one can start either with hydantoin or 2-thiohydantoin. It was our experience, however, that it is more practical to start with hydantoin and prepare the cinnamalhydantoin by direct condensation. Both the cinnamalhydantoin (XIII) and the thiohydantoin (XXI) behave in an analogous manner when reduced in alkaline solution with sodium amalgam. The corresponding hydantoic acids, which are represented by Formulas XIV and XXII, respectively, were formed. The corresponding hydantoins (XVIII) and (XXIII) were easily obtained by digesting their respective hydantoic acids with hydrochloric acid. The unsaturated thiohydantoin (XXIII) was easily desulfurized by digestion with chloroacetic acid and transformed into the hydantoin (XVIII).

The hydantoic acid (XIV) is very stable in the presence of alkalis. However, it slowly underwent decomposition when digested for a long time with strong, aqueous, barium hydroxide solution and was transformed into the α -amino acid (XV). This new amino acid dissolves in about 100 parts of boiling water and separates, on cooling, in beautiful, colorless, distorted needles which are tasteless. It is very soluble in alcohol and melts at 247-248° with decomposition. The yield of pure amino acid formed by hydrolysis was 82% of the theoretical,

¹ *Ann. Chem. J.*, 45, 446 (1911).

² *Loc. cit.*

³ Johnson and Hadley, *THIS JOURNAL*, 37, 171 (1915); Johnson and Bates, *Ibid.*, 37, 383 (1915).

while the yield of the acid, if based on the quantity of hydantoin originally used in its synthesis, was only about 25% of theory.

The α -amino acid (XV) reacts normally with ammonium thiocyanate, in the presence of acetic anhydride,¹ forming nearly quantitatively the acylthiohydantoin (XIX). The latter was converted, by hydrolysis with hydrochloric acid, into the same 2-thiohydantoin (XXIII) as was formed by digesting the thiohydantoic acid (XXII) with hydrochloric acid.

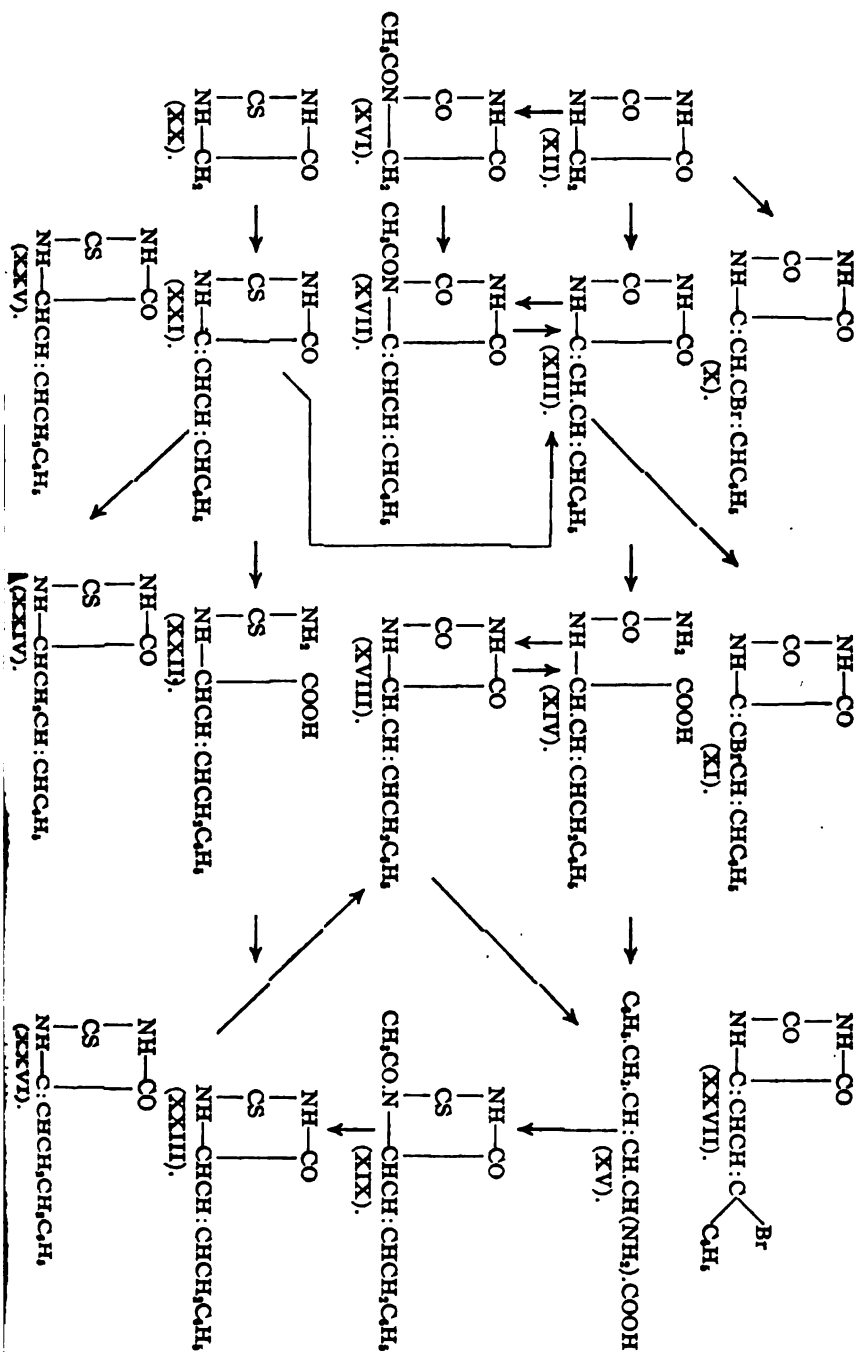
We also investigated the behavior of 2-thio-4-cinnamalhydantoin (XXI) when digested in acetic acid with zinc dust. Under these conditions the hydantoin (XXIII) was not produced, but another product was formed whose constitution has not yet been established. The loss of yellow color on reduction indicates a destruction of the double bond in position 4 of the hydantoin. Whether this double bond is reduced independently, as in the case of other aldehyde-condensation products, forming the hydantoin (XXIV), or whether the change actually involves an addition of hydrogen at the Thiele 1,4-union in the hydantoin (XXI), giving a stereoisomer (XXV), remains to be decided. The third possible isomer represented by Formula XXVI should be formed by condensation of 2-thiohydantoin with phenylpropylaldehyde. A complete investigation of these interesting changes will be carried out at a future date.

Especially interesting was the behavior of cinnamalhydantoin (XIII) towards acetic anhydride. It has been our previous experience that aldehyde condensation products of this type have not shown a tendency to interact with acetic anhydride. We now find that this compound (XIII), is transformed by the action of this reagent into the corresponding acetylhydantoin represented by Formula XVII. The yield was excellent. The structure of this compound was established by the fact that the same hydantoin was formed by condensation of Siemonsen's² 3-acetylhydantoin with cinnamaldehyde. 4-Cinnamalhydantoin (XIII), does not add bromine in acetic acid solution to form a saturated compound or a dibromoderivative. On the other hand, it interacts with the halogen in a similar manner as does benzalhydantoin,³ and forms a monobrom substitution product with evolution of hydrobromic acid. We have represented this hydantoin by Formula XI. The same hydantoin is also formed by treatment of the hydantoin (XIII) with an excess of bromine. That the bromine does not substitute in the β -position was established by the fact that a different bromohydantoin (X) was formed

¹ Johnson and Nicolet, *THIS JOURNAL*, 33, 1973 (1911); Johnson, *Am. Chem. J.*, 49, 68 (1913).

² *Ann.*, 333, 111 (1904).

³ Wheeler, Hoffmann and Johnson, *J. Biol. Chem.*, 10, 147 (1911).



by condensation of bromocinnamic aldehyde¹ $C_6H_5CH : CBrCHO$ with hydantoin. The only other monobromo derivative theoretically possible, if we disregard those where the halogen is substituted in the benzene ring, would be the bromohydantoin represented by Formula XXVII. This we have temporarily eliminated because it seems very improbable that bromine would substitute in a propenyl grouping on the carbon joined to phenyl. In other words, the interesting results which we have obtained is not what would be expected if the 1,4-union in the hydantoin (XIII), interacted with bromine in accordance with Thiele's law. The study of these compounds will be continued.

The various transformations discussed above are represented by the preceding structural formulas.

Experimental Part.

4-Cinnamal Hydantoin (XIII).—This hydantoin is easily obtained according to the following procedure: A mixture of 10 g. of hydantoin, 14 g. of cinnamic aldehyde, 50 g. of fused sodium acetate and 50 cc. of glacial acetic acid are heated for 6 hours in an oil bath at 130–140°. The resulting product is then cooled and finally warmed with 500 cc. of water until thoroughly disintegrated, in order to dissolve all the sodium acetate. The hydantoin is insoluble in the water and separates as a brown crystalline powder. The yield of crude material is generally about 15.5 g. or 72% of the theoretical. The hydantoin is easily purified by crystallization from hot, glacial acetic acid and separates, on cooling, as clusters of canary yellow prisms which melt at 272–273° to a red oil with decomposition. The hydantoin crystallizes from 95% alcohol in stout prisms or long, slender prisms, depending on the strength of the solution and the temperature of crystallization. The compound is insoluble in water and very difficultly soluble in ether. Analysis:

Calc. for $C_{12}H_{10}O_2N_2$: N, 13.08. Found: N, 12.95, 13.12.

γ -Phenylpropenylhydantoic Acid (XIV).—This acid is formed by reduction of the above hydantoin with sodium amalgam. Eight and two tenths grams of the preceding hydantoin were dissolved in a solution containing 2.5 g. of potassium hydroxide in 100 cc. of water. After diluting further with 260 cc. of water and warming to 60–65°, 110 g. of 3% sodium amalgam were added slowly, keeping the temperature of the solution between 50–65°. After heating for 1.5 hours the reduction was complete, and no cinnamalhydantoin separated on acidifying the solution with hydrochloric acid. During the reduction, the color of the solution changed from yellow to pale green. The fluid was decanted from mercury, cooled and finally acidified with hydrochloric acid, when the hydantoic acid separated. The yield was 7.0 g. This acid is very soluble in hot water and alcohol. It was purified for analysis by recrystallization.

¹ Zincke and Hagen, *Ber.*, 17, 1814 (1884).

tion from hot water and separated in the form of colorless, diamond-shaped plates which melted from $142-161^{\circ}$ with decomposition. The melting point is very indefinite and varies according to the rate of heating. An attempt to reduce cinnamalhydantoin with stannous chloride and hydrochloric acid was unsuccessful.

Calc. for $C_{12}H_{14}O_2N_2$: N, 11.86. Found: N, 11.80, 11.94.

α -Amino- δ -phenylpentenic Acid, $C_6H_5CH_2CH:CH.CH(NH_2)COOH$.—This new α -amino acid was obtained by digesting the 7.0 g. of the hydantoic acid, described above, with 50 g. of barium hydroxide in 200 cc. of water for 50 hours. After this treatment the hydrolysis was complete and no ammonia was evolved. Then 150 cc. of water were added and the solution boiled to dissolve all the amino acid. After filtering from barium carbonate the excess of barium was precipitated as barium sulfate by adding the required amount of sulfuric acid. The solution, freed from sulfate and barium, was then concentrated to a volume of about 150 cc. and cooled, whereupon practically all of the amino acid present separated in a crystalline condition. It was purified by crystallization from boiling water, a little bone-coal being added to remove all color. It crystallized in long, colorless needles which melted at $247-248^{\circ}$ to a yellow oil with some decomposition. The acid is very soluble in alcohol and dissolves in about 100 parts of boiling water.

Calc. for $C_{11}H_{14}O_2N$: N, 7.25. Found: N, 7.17, 7.26.

4-(γ -Phenylpropenylhydantoin) (XVIII).—This hydantoin is formed smoothly by digesting the above hydantoic acid with hydrochloric acid. One hour's boiling with 25% hydrochloric acid is sufficient to close the ring. The hydantoin crystallizes from 95% alcohol in long needles which melt at $160-161^{\circ}$ to a clear oil without effervescence.

Calc. for $C_{12}H_{14}O_2N_2$: N, 12.84. Found: N, 12.67, 12.79.

2-Thio-3-acetyl-4-(γ -phenylpropenyl)-hydantoin (XIX).—Two grams of α -amino- δ -phenylpentenic acid were warmed on the steam bath with 2 g. of dry ammonium thiocyanate and 10 cc. of acetic anhydride for one hour at 100° . The orange-colored solution which was obtained, was then allowed to stand over night when this acetylhydantoin separated in the form of yellow prisms. The yield was 2.5 g., being equivalent to 90.5% of theory. It was purified by recrystallization from 80% alcohol, using enough of the solvent so that crystallization did not commence above the room temperature. The compound always separated as an oil if the solution was too concentrated. The hydantoin crystallized in orange-colored plates which melted at $97-98^{\circ}$ to an oil without effervescence. It was difficultly soluble in water and quite soluble in alcohol and ether.

Calc. for $C_{14}H_{16}O_2N_2S$: N, 10.14. Found: N, 10.03, 9.95.

2-Thio-4-(γ -phenylpropenyl)-hydantoin (XXIII).—In order to obtain this hydantoin the above acetyl derivative was suspended in strong hydrochloric acid and the mixture heated on a steam bath until the acid was expelled by evaporation. This operation was repeated four times, in order to insure complete hydrolysis, when the thiohydantoin was obtained as a brittle, orange-colored product melting at $124-125^{\circ}$ to a turbid oil. This material was insoluble in water, but very soluble in alcohol. It could not be crystallized from 95% alcohol, for even on spontaneous evaporation of the solvent at room temperature it deposited in the form of a gum. From 60% alcohol it separated on slow cooling, in the form of cream-colored plates. More of this same material was obtained by mixing the alcohol filtrate with hydrochloric acid and evaporating to dryness. When perfectly pure the thiohydantoin crystallizes from dilute alcohol as needles or distorted prisms which melt at $126-127^{\circ}$ to an oil. A mixture of this hydantoin and the corresponding acetyl compound melted at 85° .

Calc. for $C_{12}H_{14}ON_2S$: N, 11.96. Found: N, 11.78, 11.76.

Desulfurization of 2-Thio-4-(γ -phenylpropenyl)-hydantoin (XXIII) with Formation of 4-(γ -phenylpropenyl)-hydantoin (XVIII).—This change can be accomplished easily by heating the thiohydantoin with a 10% aqueous solution of chloroacetic acid at 140° for 4 hours. Under these conditions the sulfur is completely removed and, on cooling, the acid solution, the hydantoin is obtained in the form of needles which melt at 160° . The operation of boiling the thiohydantoin with chloroacetic acid was not effective in removing the sulfur.

2-Thio-4-cinnamylhydantoin (XXI).—Eight grams of 2-thiohydantoin which were prepared according to the method of Johnson and Nicolet, were heated with 8.5 g. of cinnamic aldehyde, 40 g. of fused sodium acetate and 60 cc. of glacial acetic acid for 2 hours at 130° . The resulting mixture was then cooled and the solid mixture warmed with 400 cc. of water until completely disintegrated. The hydantoin was obtained as a brownish yellow product insoluble in water. The yield of crude material was 13 g. or 85% of the theoretical. It was purified for analysis by crystallization from glacial acetic acid and melted at $262-263^{\circ}$.

It was noticed that this material, on crystallization from the acetic acid separated, while the solution was very hot, in the form of red, prismatic columns but after the temperature of the solution had fallen below 70° it then deposited in long, slender, yellow needles. By proper regulation of the temperature and application of fractional crystallization it was possible to separate the two forms.

The red product melted at $262-263^{\circ}$ to an oil without apparent decomposition and was identified as 2-thio-4-cinnamylhydantoin (XXI).

¹ *Loc. cit.*

On drying for 2 hours at 125° it lost only 0.1% of its weight. It was insoluble in water and soluble in alcohol. It was less soluble in alcohol and glacial acetic acid than the cinnamalhydantoin.

Calc. for $C_{12}H_{10}ON_2S$: N, 12.17. Found: N, 11.98.

On taking the melting point of the yellow modification it was noticed that it turned red at about 140 to 160° and then melted at the same temperature as the red compound, namely, 262 – 263° . In fact, the yellow form was identified as the red hydantoin containing acetic acid of crystallization. A sample of the yellow modification, which was washed with ether and then dried at ordinary temperature, gave the following results on analysis:

Calc. for $C_{12}H_{10}ON_2S \cdot CH_3COOH$: N, 9.65. Found: N, 9.59, 9.68.

After drying at 125° for 3 hours and finally for 4 hours at 145° the hydantoin was then analyzed for nitrogen when the following results were obtained:

Calc. for $C_{12}H_{10}ON_2S$: N, 12.17. Found: N, 11.93, 12.03.

From these results it is evident that the yellow modification of the thiohydantoin contains one molecule of acetic acid of crystallization.

Reduction of 2-Thio-4-cinnamalhydantoin with Sodium Amalgam. γ -Phenylpropenylthiohydantoic Acid (XXII).—Two grams of the thio-cinnamalhydantoin were dissolved in the least possible amount of 10% sodium hydroxide solution and enough water was added to bring the volume up to 150 cc. The temperature of this solution was then kept between 65 – 75° and the hydantoin reduced by adding 100 g. of 3% sodium amalgam in small portions at a time. The color of the solution changed from orange to an apple green during this operation. After the reaction was complete the solution was then acidified with hydrochloric acid, when this hydantoic acid separated as an oil. Hydrogen sulfide was also evolved indicating partial decomposition. The hydantoic acid showed no tendency to crystallize on long standing. It was dissolved in ether, dried and the solvent allowed to evaporate spontaneously, but even after such treatment only a gum was obtained, which refused to crystallize after standing for 2 weeks. Its constitution was established by the fact that it was converted into the corresponding hydantoin by digestion with hydrochloric acid. This was accomplished by suspending the hydantoic acid in strong hydrochloric acid and heating on the steam bath to remove the hydrochloric acid. After repeating this treatment 3 times we finally obtained the thiohydantoin, which deposited as a brittle, resinous product melting at 120 – 130° . It was purified by crystallization from 50% alcohol and separated in cream-colored crystals which melted at 127° without effervescence. A mixture of this substance with some 2-thio-4-(γ -phenylpropenyl)-hydantoin, described above, melted at the same temperature.

2-Thio-4-(γ -phenylallyl)-hydantoin? (XXIV).—This was obtained by partial reduction of 2-thio-4-cinnamalhydantoin. Two and one-half grams of the cinnamalhydantoin were dissolved in sufficient glacial acetic acid to form a clear solution at 65°; 20 g. of zinc dust were added and the solution then warmed for 1.5 hours at 65–75°. It was found that boiling the solution caused an evolution of hydrogen sulfide. During the first half hour the color of the solution changed from chrome yellow to pale apple green, but after this no further color change was noticed. After the reduction was complete the acid solution was cooled and filtered into an excess of cold dilute hydrochloric acid, whereupon this unsaturated hydantoin separated at once as a salmon-colored, curdy precipitate. This substance was dissolved again in pure acetic acid and the precipitation with hydrochloric acid repeated in order to remove all traces of zinc. The hydantoin was extremely soluble in all the common organic solvents. It was finally dried at 40° and then heated for an hour at 100° when it was obtained as a powder having no definite melting point. The substance began to contract at 175°, when heated in a capillary tube, giving red gum at 185° which became partially fluid at 190°. The yield was quantitative. The compound immediately decolorized a dilute acetone solution of potassium permanganate showing the presence of an unsaturated grouping.

Calc. for $C_{13}H_{13}ON_2S$: N, 12.07. Found: N, 11.87, 11.76.

Desulfurization of 2-Thio-4-cinnamalhydantoin with Formation of 4-Cinnamalhydantoin.—An attempt was made to desulfurize this 2-thio hydantoin by boiling 2.5 g. of the compound for 6 hours with 5 g. of chloroacetic acid in 50 cc. of water. The hydantoin did not dissolve and as there was no change in its appearance by this treatment 5 g. more of chloroacetic acid were added and the digestion continued for 14 hours. Even after this prolonged treatment the hydantoin had undergone no change and melted at 253°. The hydantoin was then heated in a bomb tube for 6 hours with 7 g. of chloroacetic acid (4 molecular proportions) and 15 cc. of water. On opening the tube there was no pressure and the cinnamalhydantoin was suspended in the acid solution. This was separated by filtration, dissolved in dilute sodium hydroxide solution and finally precipitated by addition of hydrochloric acid. The hydantoin was then purified by crystallization from glacial acetic acid. It melted at 272–273° to a red oil with effervescence. It gave no test for sulfur.

The Action of Bromine on 4-Cinnamalhydantoin, 4-(α -Bromocinnamal)hydantoin (XI).—One and five-tenths grams of the cinnamalhydantoin were dissolved in 200 cc. of glacial acetic acid and the temperature of the mixture kept at 50–60° while the calculated amount of bromine vapor (1.12 g.) was aspirated through the solution. After the bromine had been completely absorbed, the excess of acetic acid was removed by evaporation.

ting under diminished pressure and the solution cooled, when the bromohydantoin separated in the form of yellow needles which were purified by recrystallization from acetic acid. The substance melted at 290–295° with decomposition. This melting point is not definite and varies according to the rate of heating. The hydantoin is insoluble in water and moderately soluble in alcohol.

Calc. for $C_{12}H_9O_2N_2Br$: N, 9.55. Found: N, 9.20, 9.26.

In a second experiment 2 g. of 4-cinnamalhydantoin were dissolved in 200 cc. of glacial acetic acid and 4 molecular proportions of bromine (3 g.) aspirated through the solution. The same temperature conditions were maintained as in the first experiment. There was a large excess of bromine which did not react with the hydantoin. This was expelled with the excess of acetic acid by heating under diminished pressure. On cooling we obtained the same compound as was formed in our first experiment, namely, *bromocinnamalhydantoin*. In other words, there was no tendency for the bromine to add at the double bond of the allyl group. After crystallization from glacial acetic acid the compound melted at 290–295° with decomposition.

Calc. for $C_{12}H_9O_2N_2Br$: N, 9.55. Found: N, 9.34, 9.36.

4-(β -Bromocinnamal)-hydantoin (X).—This hydantoin was prepared by condensing bromocinnamic aldehyde¹ with hydantoin. The following proportions were used: 10 g. of the aldehyde, 5 g. of hydantoin, 25 g. of anhydrous sodium acetate, 20 cc. of glacial acetic acid and 20 cc. of acetic anhydride. After heating for 1.5 hours at 130° the mixture was then cooled and triturated with cold water when we obtained 6.0 g. of the crude hydantoin. This compound was unstable and a certain amount of decomposition always took place when attempts were made to purify it by crystallization. A product was finally isolated by crystallization from glacial acetic acid which crystallized in clusters of yellow prisms and melted at 226–227° with decomposition. Work had to be abandoned on this compound because it or the monobromocinnamic aldehyde caused acute and very painful dermatitis on the hands of the experimenter.

Calc. for $C_{12}H_9O_2N_2Br$: N, 9.55. Found: N, 9.7.

3-Acetyl-4-cinnamalhydantoin (XVII.)—It was observed during the condensation of hydantoin with cinnamic aldehyde, when some acetic anhydride was incorporated with the acetic acid, that the condensation product always contained two products, one of which was cinnamalhydantoin melting at 273° and the other a substance, which melted much lower, was more insoluble in glacial acetic acid and contained less nitrogen. It was impossible to isolate it in a pure condition. In order to determine whether this secondary product might be an acetyl derivative, 1.5 g. of the

¹ Zincke and Hagen *Loc. cit.*

cinnamalhydantoin were heated with 30 cc. of acetic anhydride for 4 hours at 140–150°. There was no apparent reaction at first but after heating for about an hour most of the hydantoin had disappeared and a new product began to deposit in the form of needles. On continued heating all the cinnamalhydantoin changed to this modification. This was identified as the acetyl derivative of cinnamalhydantoin and crystallized from glacial acetic acid as yellow prisms, which melted at 241–242° without any apparent decomposition. This hydantoin was less soluble in glacial acetic acid than cinnamalhydantoin.

Calc. for $C_{14}H_{13}O_4N_2$: N, 10.94. Found: N, 10.96, 10.94.

This hydantoin easily underwent hydrolysis when warmed with hydrochloric acid was changed into cinnamalhydantoin. This was crystallized from glacial acetic acid and melted at 272–273° with decomposition.

In order to determine whether the acetyl group in this new hydantoin was linked to the 1- or 3-position of the ring 3-acetylhydantoin¹ (XVI) was condensed with cinnamic aldehyde by heating in the presence of sodium acetate, acetic acid and acetic anhydride. After heating for 3.5 hours at 130–135° the fused mass was cooled and then triturated with 500 cc. of cold water when the above acetylhydantoin separated in a crystalline condition. The yield was excellent. It was purified by crystallization from acetic acid and melted at 241–242°. A mixture of this substance with some of the acetyl compound described above melted at the same temperature.

Calc. for $C_{14}H_{13}O_4N_2$: N, 10.94. Found: N, 10.9.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

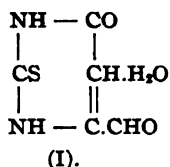
RESEARCHES ON PYRIMIDINES. LXXV. PYRIMIDINE ALDEHYDES AND THEIR BIOCHEMICAL INTEREST (THIOURACILALDEHYDE).

By TREAT B. JOHNSON AND LEONARD H. CRETCHER, JR.

Received July 5, 1915.

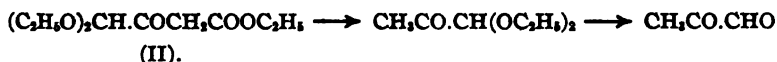
So far as the writers are aware, no cyclic aldehydes of the pyrimidine series have been described in the literature. Such unsaturated combinations should manifest great reactivity and consequently a knowledge of their chemistry is especially desirable, because of the probability that they will prove of value for the future synthesis of new pyrimidine combinations of great biochemical interest. A description of three aldehydes of this series of cyclic compounds will be given in this paper. One of these, 2-thiouracil-4-aldehyde (I), can be obtained easily in quantity for synthetical work.

¹ Siemonsen, *Loc. cit.*



Our pyrimidine-nucleoside investigations have, so far, been practically confined to the study of uracil combinations containing simple mono-atomic, alcohol groupings in the 4-position of the pyrimidine ring.¹ Our method of synthesizing such combinations is somewhat limited in its utility, because it is dependent on the use of characteristic β -ketone esters of definite structure. Most of these esters required for our work are unknown and many of them would be extremely difficult to synthesize in quantity.² It became necessary, therefore, as our work developed, to obtain, if possible, uracil combinations (or thiouracil) containing a grouping in the 4-position, which could be utilized for side-chain construction. A grouping was desired which would render possible the synthesis indirectly of glycol and higher alcohol combinations. Such a radical is the aldehyde group $-\text{CHO}$, which we have now been able to introduce into the pyrimidine ring according to the method described below.

Among the aliphatic esters which have been observed to condense with ethyl acetate, in the presence of sodium, to form β -ketone esters (Claisen's condensation), is the ethyl ester of diethoxyacetic acid $(\text{C}_2\text{H}_5\text{O})_2\text{CH}.\text{COOC}_2\text{H}_5$. Dakin and Dudley³ have shown that these two aliphatic esters interact smoothly under specific conditions, forming the new β -ketone ester (II). This compound and its α -carbon substituted derivatives are characterized by their behavior on hydrolysis. They exhibit the normal behavior of β -ketone esters and can be transformed into ketone acetals. The latter on hydrolysis with acids are easily transformed into glyoxals. The complete hydrolysis of ethyl γ -diethoxyacetoacetate (II) may be expressed in the following manner:



We have now incorporated this characteristic β -ketone ester into our nucleoside work⁴ and find that it condenses normally with thiourea in

¹ See our pyrimidine papers.

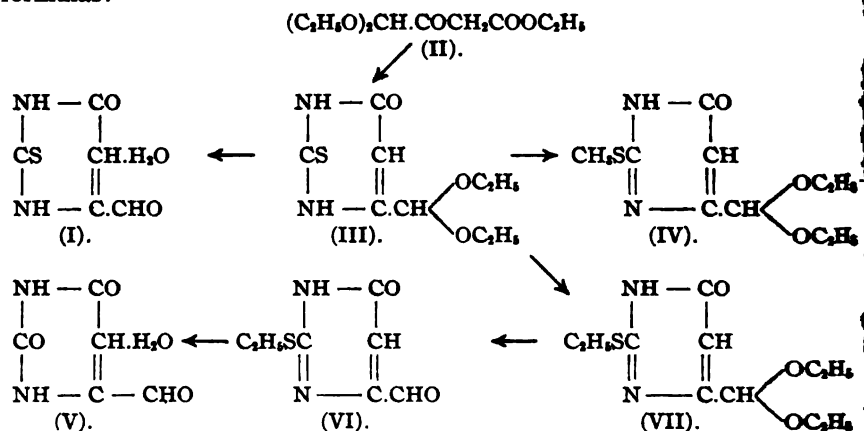
² Work is now in progress, in this laboratory, dealing with the synthesis of various representatives of new types of β -ketone esters. This investigation involves the application of Claisen's reaction with types of esters, which hitherto have not been studied, and new combinations have been obtained which are of great value for future syntheses. (T. B. J.)

³ *J. Chem. Soc.*, 105, 2453 (1914).

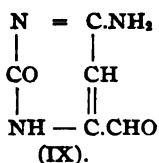
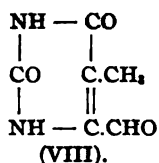
⁴ So far as we are aware the behavior of ethyl triethoxyacetate $(\text{C}_2\text{H}_5\text{O})_3\text{C}.\text{COOC}_2\text{H}_5$ towards ethylacetate in the presence of sodium has not been investigated. (T. B. J.)

alcohol solution, and in the presence of sodium ethylate, forming the pyrimidine-acetal represented by Formula III. The acetal grouping in this pyrimidine exhibits a normal behavior. It is stable in the presence of alkali, but undergoes hydrolysis with mineral acids, and is transformed quantitatively into the aldehyde of 2-thiouracil represented by Formula I. The sodium salt of the thiopyrimidine (III) behaves in a regular manner when allowed to interact with alkylhalides. Alkylation takes place with substitution upon the sulfur atom and the corresponding mercaptopyrimidines are formed quantitatively. We have prepared by the action of methyl iodide and ethyl bromide the two mercaptopyrimidines represented by Formula IV and VII, respectively.

The mercaptopyrimidine (VII) behaves in an interesting manner when subjected to hydrolysis with hydrochloric acid. If the action is not allowed to become too vigorous, only the acetal grouping is destroyed and the corresponding mercaptopyrimidinealdehyde (VI) is formed. If, however, the pyrimidine (VII) is subjected to very vigorous treatment with strong hydrochloric acid, the reaction proceeds further. Mercapturic acid is then also evolved and the final product of the reaction is uracilaldehyde represented by Formula V. Attempts to prepare this aldehyde (V) by desulfurization of the corresponding thiouracilaldehyde (I) have, thus far, been unsuccessful. Very little attention has been paid to the chemistry of uracilaldehyde (V), but a careful study of its properties and reactions will be taken up the coming year. The various changes, which have been discussed above, are expressed by the following structural formulas:



We ask that the investigation of pyrimidine aldehydes be reserved for this laboratory. Attempts will be made to synthesize the two unknown aldehyde derivatives of thymine and cytosine, which are represented by Formulas VIII and IX, respectively.



Experimental Part.

Preparation of Dichloroacetic Acid, $\text{Cl}_2\text{CH} \cdot \text{COOH}$.—All the dichloroacetic acid which was used in this investigation was made from chloral hydrate. The procedure was to convert the chloral into the potassium salt of the halogen acid by digesting it with potassium ferrocyanide according to Wallach's¹ directions, and then decompose the potassium salt with hydrochloric acid.

Our method of obtaining the free acid from its potassium salt is illustrated by a description of one experiment: 180 g. of the potassium salt were suspended in 600 cc. of dry benzene and the salt decomposed by passing a stream of dry hydrochloric acid gas through the mixture until completely saturated. It was thoroughly shaken at times in order to produce a thorough decomposition. After the salt was completely decomposed the insoluble potassium chloride was filtered off by suction and the benzene removed by heating the mixture finally up to 150° in an oil bath. The dichloroacetic acid was then distilled at ordinary pressure, when we obtained 105 g. of the acid boiling at $188\text{--}192^\circ$. This was a yield of 76% of the theoretical. In another experiment we obtained 67 g. of the acid from 100 g. of the potassium salt, which is a yield of 87% of the theoretical.

Ethyl Diethoxyacetate, $(\text{C}_2\text{H}_5\text{O})_2\text{CH} \cdot \text{COOC}_2\text{H}_5$.²—A description of one experiment will illustrate our procedure for making this ester: Three molecular proportions of sodium (56.2 g.) were dissolved in 800 cc. of ethyl alcohol, which had previously been desiccated by distillation over metallic sodium. The flask containing the ethylate solution was then connected with a reflux condenser and the solution heated to 80° in a water bath. While maintaining the temperature at 80° , 105 g. of dichloroacetic acid were added slowly by means of a dropping funnel. There was an immediate reaction with formation of sodium chloride and the sodium salt of diethoxyacetic acid. After the reaction was complete the solution was then cooled and exactly 35 g. of hydrochloric acid, in absolute alcohol solution, added cautiously while holding the temperature of the solution below 10° . This is approximately 0.2 of a mol in excess of the amount of acid required to liberate the diethoxyacetic acid, or 5.8 g. of hydrochloric acid. The alcoholic solution was then allowed to stand for 15–18 hours at room temperature to effect a thorough esterification.

¹ Ber., 10, 1525 (1877).

² Wohl and Lange, Ber., 41, 3612 (1908).

The hydrochloric acid was then exactly neutralized cold by adding the required amount of sodium ethylate in alcohol solution and the undissolved sodium chloride separated by filtration. We obtained a clear, yellow solution which was heated at 30–35° under diminished pressure to remove all the alcohol. The red syrupy liquid which was obtained, was then diluted with 20 cc. of cold water and a large volume of ether added when we obtained 75 cc. of material immiscible with the solvent. The ether extract was saved and the immiscible liquid extracted repeatedly with fresh ether until the volume finally remained constant at 55 cc. (see below).

The ethereal solution was dried over sodium sulfate and, after removal of the ether, the oil was distilled under diminished pressure. We obtained 48 g. of the ester boiling from 94.5–98° at 19 mm. pressure and about 10 g. boiling somewhat higher, 98–103° at 20–21 mm. pressure. There were about 12 g. of a higher fraction with indefinite boiling point.

The immiscible liquid (55 cc.) mentioned above was dark red in color and very viscous. It was covered with ether and hydrochloric acid cautiously added, when the red color disappeared and an oil dissolved in the ether. This was thoroughly extracted and the ether dried over calcium chloride for 24 hours. On evaporating the solvent we obtained 48 g. of crude diethoxyacetic acid. This was esterified by dissolving it in 72 g. of absolute alcohol containing 2.5 g. of hydrochloric acid and allowing the solution to stand for several hours. The hydrochloric acid was then neutralized with the required amount of sodium ethylate and the ester separated in the usual way. We recovered here 12 g. of pure ester boiling at 83–85° under a pressure of 13 mm. The total yield of ester was 70 g. or 50% of the theoretical.

Ethyl γ -Diethoxyacetoacetate (II).—This ester has previously been described by Dakin and Dudley¹ who have assigned to it a boiling point of 112° at 4–6 mm. pressure. We prepared the ester according to their method with slight modifications. These changes were made after we found it was not necessary to obtain the pure β -ketone ester for our work. We proceeded as follows: The following proportions were taken: 65 g. of ethyl diethoxyacetate, 26 g. of metallic sodium in wire form and 100 g. of ethyl acetate. The ethoxy ester and one-half of the acetate were mixed in an Erlenmeyer flask, connected to a reflux condenser, and the mixture heated to 80°. One-half of the sodium was then introduced in small portions at a time. Heating was continued, and in about 3 hours the sodium had completely dissolved. The remainder of the ethylacetate was then added and finally, in small amounts at a time, the rest of the sodium. Heating was then continued for 4 hours, when the sodium had practically all disappeared and then reaction was apparently complete.

¹ Dakin and Dudley, *Loc. cit.*

The resulting mixture was then cooled and carefully mixed with ice water. The unaltered esters were first removed by extraction with ether and the clear aqueous solution acidified cold with hydrochloric acid to liberate the β -ketone ester from its sodium salt. This ester was extracted with ether and the solution desiccated by allowing it to stand over anhydrous sodium sulfate. After removal of the ether the β -ketone ester was obtained as a red oil. This was not distilled but was heated in an oil bath at 145° under a pressure of 23 mm. in order to expel any ethyl acetoacetate that was present. The product left behind after this treatment weighed 65 g. From 86 g. of $(C_2H_5O)_2CHCOOC_2H_5$ Dakin and Dudley obtained 76 g. of the pure β -ketone ester.

The Diethylacetal of 2-Thio-4-uracilaldehyde (III).—For the preparation of this new pyrimidine the following proportions were taken:

65 g. of the undistilled β -ketone ester described above, 10.5 g. of sodium, 40 g. of thiourea and 200 cc. of absolute alcohol. The sodium was first dissolved in the alcohol and the thiourea then dissolved in the resulting solution. Finally the β -ketone ester was added and then 50 cc. more of alcohol. The mixture was then heated on a steam bath for 7 hours after which the mixture was transferred to a casserole and the alcohol evaporated by heating at 100° . The residue, which remained behind, was black and very viscous. This was dissolved in 275 cc. of water, and the solution digested with bone coal, when a clear, dark red solution was obtained. This was cooled and acidified cautiously with dilute hydrochloric acid. At first the pyrimidine separated as a thick oil, but soon assumed a granular condition on stirring. The product was dried in a desiccator over sulfuric acid and weighed 52 g. The crude material melted at 150° . The acetal was purified by crystallization from 95% alcohol and separated in thick, rhombic blocks which melted at 160° . The compound is sparingly soluble in water and soluble in cold hydrochloric acid.

Calc. for $C_8H_{14}O_3N_2S$: N, 12.17. Found: N, 12.16, 12.12.

This pyrimidine was not desulfurized by digesting in alcohol solution with mercuric oxide. Freshly precipitated lead hydroxide was also used, but here also there was only slight evidence of the formation of lead sulfide. Attempts to desulfurize the pyrimidine by warming with chloroacetic acid were unsuccessful.

2-Thio-4-uracilaldehyde (I).—A quantitative yield of this interesting pyrimidine is obtained by hydrolysis of its acetal with hydrochloric acid. Three grams of the thioacetal (above) were dissolved in about 100 cc. of dilute hydrochloric acid and the solution finally heated to boiling. On cooling, the aldehyde separated in the form of golden-yellow, glistening plates, which darkened at about 230° and then decomposed at 250° . The melting point was not altered by further crystallization from dilute

hydrochloric acid. The aldehyde reduces silver nitrate in ammoniacal solution and also Fehling's solution. It dissolves easily in alcohol and glacial acetic acid. It behaves peculiarly when warmed with water. It dissolves in this solvent, but on cooling separates as a tarry product. The addition of water to an acetic acid solution of the aldehyde produces the same tarry precipitate. The aldehyde contained one molecule of water of crystallization, which was not completely expelled until the pyrimidine was heated to 160–170°.

Calc. for $C_8H_8O_2N_2S \cdot H_2O$: N, 16.08; H_2O , 10.36. Found: N, 16.04; H_2O , 10.17.

Phenylhydrazone of the Thiouracil Aldehyde.—A small quantity of the aldehyde was dissolved in dilute hydrochloric acid and sodium acetate and phenylhydrazine added to the solution. The hydrazone separated at once as yellow needles which did not melt below 300°. This compound is insoluble in alcohol, benzene, petroleum ether and only slightly soluble in water. Analysis (Dumas' method):

Calc. for $C_{11}H_{10}ON_2S$: N, 22.7. Found: N, 22.33.

Diethyl Acetal of 2-Ethylmercapto-6-oxy-4-aldehydopyrimidine (VII).—For the preparation of this new pyrimidine the following reagents were used: 10 g. of the corresponding 2-thiopyrimidine (above), 1 g. of sodium, 1.2 g. of ethyl bromide and 250 cc. of alcohol. The sodium was first converted into sodium ethylate by dissolving in the alcohol and the thiopyrimidine then dissolved in this solution. The ethyl bromide was then added and the solution heated on the steam bath for 1 hour when the alkylation was complete. The alcohol was then evaporated and the residue triturated with water to remove the salt when the pyrimidine was obtained in a crystalline condition. It was purified by crystallization from hot water and separated in the form of colorless, slender needles which melted at 128° to an oil. The yield of pyrimidine was 11 g. The compound is very soluble in alcohol and benzene.

Calc. for $C_{11}H_{16}O_2N_2S$: N, 10.85. Found: N, 10.65.

Diethyl Acetal of 2-Methylmercapto-6-oxy-4-aldehydopyrimidine (IV).—Obtained by alkylation of the corresponding 2-thiopyrimidine with methyl iodide. The yield was practically quantitative. The pyrimidine was purified for analysis by recrystallization from alcohol and separated in the form of needles which melted at 133° to a clear oil.

Calc. for $C_{10}H_{16}O_2N_2S$: N, 11.4. Found: N, 11.20.

2-Ethylmercapto-6-oxy-4-aldehydopyrimidine (VI).—This is formed by careful hydrolysis of its corresponding acetal. Two grams of the latter were dissolved in 100 cc. of hydrochloric acid (equivalent parts of water and concentrated acid) and the solution evaporated on the steam bath until crystals made their appearance on the surface of the liquid. This condition was reached at a volume of

about 20 cc. On cooling more of the same material separated. This was identified as the mercaptoaldehyde and melted at 145° . It crystallized in elongated prisms which were soluble in hot water and dilute hydrochloric acid and sparingly soluble in alcohol. The aldehyde reduced silver nitrate in ammoniacal solution and gave a crystalline hydrazone. Analysis:

Calc. for $C_7H_8O_2N_2S$: N, 15.16. Found: N, 15.06.

Uracil-4-aldehyde (V).—This aldehyde has not been subjected to investigation and consequently we shall only mention here a single experiment in which the pyrimidine was obtained. One gram of the above 2-ethylmercaptopyrimidineacetal was heated with boiling hydrochloric acid for one-half hour and the solution then evaporated practically to dryness. On cooling the remaining liquid, this pyrimidine separated as a white powder which was crystallized from dilute hydrochloric acid. It separated in small distorted prisms arranged in rosetts which did not melt at 300° . It did not respond to a test for sulfur and contained a molecule of water of crystallization, which was removed by heating the pyrimidine at 130° .

Calc. for $C_6H_4O_2N_2$: N, 17.7; H_2O , 11.39. Found: N, 17.45; H_2O , 11.30.

This pyrimidine will be subjected to a thorough investigation.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXXVI. NEW METHODS OF SYNTHESIZING 2-KETOPYRIMIDINES AND THEIR SULFUR ANALOGS.

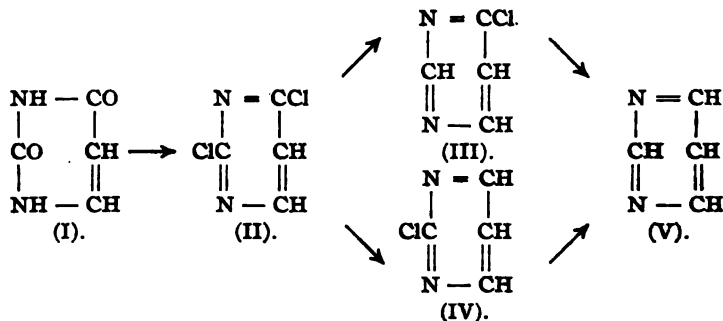
By TRENT B. JOHNSON AND A. WILLARD JOYCE.

Received July 5, 1915.

Although the chemistry of the 2,6-dioxypyrimidines, of which uracil (I), is the prototype, has been the subject of extended investigation largely on account of the ready accessibility of such substances and their biochemical interest, that of the *mono*-ketopyrimidines and the simple pyrimidine compounds has received comparatively little attention, and it was with the view of filling this gap and partly with definite synthetical aims that the preliminary work discussed in this paper was instituted.

The 2,6-dioxypyrimidines (I) are easily transformed into their corresponding dichloropyrimidines (II) by interaction with phosphorus pentachloride and phosphorus oxychloride. The yields of these dihalides are good and consequently they are available in quantity for synthetical purposes. When such halogenated pyrimidines are subjected to reduction, different intermediate products can theoretically be formed before complete removal of the halogen is effected. For example, reduction

can take place in the 2- or 6-positions of the pyrimidine ring with formation of two isomeric compounds, namely, a 6-chloro- or a 2-chloropyrimidine corresponding to Formulas III and IV, respectively. Which product



will be formed cannot be foretold and, consequently, the structure of each reduction product must be determined in each case examined. During the course of an investigation now in progress in this laboratory, we had occasion to apply such a reduction process with 2,6-dichloro-5-ethoxypyrimidine and obtained a crystalline monochloro derivative. It was not until we undertook to establish experimentally the structure of this substance that we realized the want of a simple and practical method of proving the constitution of such compounds. An account of a new method of proving structure, which fulfils the needs of our work, is now given below.

A dioxypyrimidine is obtained, by our method of synthesis, from its corresponding 2-thio- or 2-mercapto-6-oxypyrimidine by desulfurization with boiling chloroacetic acid or strong hydrochloric acid. For example 2-ethylmercapto-5-ethoxy-6-oxypyrimidine¹ (VIII) and the 5-ethoxyuracil² (IX) represent such a pair of compounds and the latter is easily prepared from the mercaptopyrimidine by the action of chloroacetic acid. Both of these pyrimidines interact with phosphorus halides to form the corresponding chlorides (XI) and (X). The mercaptohalide (XI) has been described by Johnson and McCollum³ and the dihalide (X) by Johnson and Guest.⁴ We now find that this mercaptopyrimidine (XI) undergoes reduction smoothly with zinc dust in dilute alcohol, giving the reduced pyrimidine (XIV), and it is on this observation that our method of proving structure is based. The dichloropyrimidine (X) is reduced according to the same procedure giving an excellent yield of a monochloro compound. With this data in hand it was only necessary to convert our chloropyrimidine into its corresponding ethylmercapto-

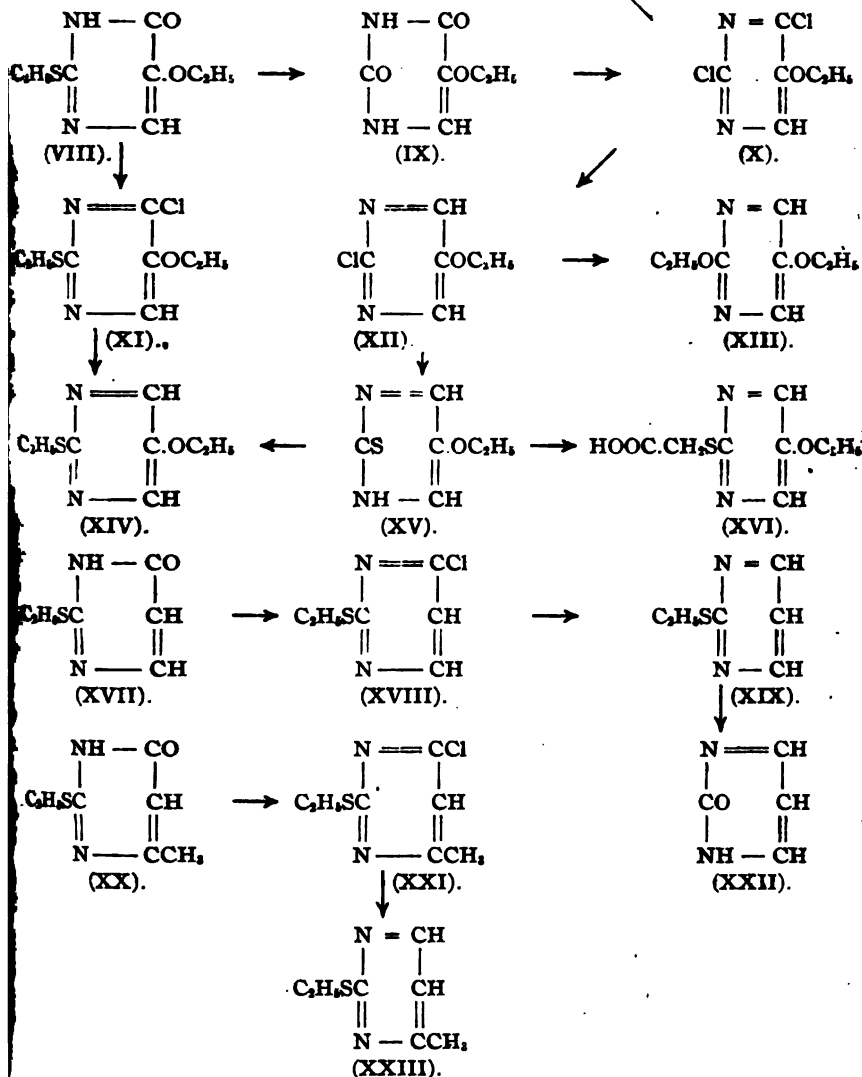
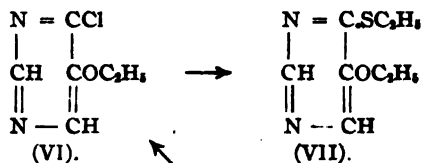
¹ Johnson and McCollum, *J. Biol. Chem.*, **2**, 441 (1906).

² Johnson and McCollum, *loc. cit.*

³ *Loc. cit.*

⁴ *Am. Chem. J.*, **42**, 284 (1909).

derivative in order to establish its constitution. Either the mercaptopyrimidine (XIV), or its isomer represented by Formula VII, should be formed. This change we have now accomplished. The chloropyrimidine



was found to interact almost quantitatively with potassium hydrogen sulfide with formation of the potassium salt of the 2-thiopyrimidine represented by Formula XV. When the latter was warmed with ethyl bromide in alcohol solution it underwent alkylation smoothly, giving the same 2-ethylmercapto-5-ethoxypyrimidine (XIV) as was obtained by reduction of the chloride (XI) with zinc dust. Therefore, the dichloropyrimidine (X) undergoes reduction in the 6-position of the ring with formation of the 2-chloro-5-ethoxypyrimidine (XII). We obtained no evidence of the formation of any 6-chloro-5-ethoxypyrimidine (VI). This method of proving constitution is characterized by its simplicity and is apparently of general application. The study of pyrimidine dihalides will be continued, and it will be interesting to determine what influence the character of the groupings substituted in positions 4 and 5 will have upon their reactivity towards reducing agents.

Having shown that the mercaptopyrimidine (XI) can be reduced with zinc dust it was important to determine whether the reaction is applicable with other mercaptopyrimidines of this type. We have now investigated the behavior towards zinc dust of 2-ethylmercapto-6-chloropyrimidine¹ (XVIII), and the corresponding 4-methylpyrimidine² (XXI), and find that both compounds are reduced smoothly to their corresponding mercaptopyrimidines represented by Formulas XIX and XXIII. In other words, these mercaptohalides behave in a similar manner towards zinc dust as their corresponding 2-anilino- and 2-methylamino representatives, which have been investigated by Johnson and Heyl³ and Johnson and Mackenzie.⁴

It is of interest to note here that Wheeler⁵ observed that 2,6-dichloropyrimidine (II) is reduced by hydriodic acid and phosphorus with formation of 6-oxypyrimidine (XXIV). In this reaction the imido-acid chloride grouping in the 1,6 positions of the ring underwent hydrolysis, while the chlorine between the two nitrogen atoms in position 2 was removed by reduction. He also made the observation that 2-amino-6-chloropyrimidine (XXV), is reduced by zinc dust to the pyrimidine (XXVI), while the isomeric 2-chloro-6-aminopyrimidine (XXVII) is not changed by this reagent. On the other hand this pyrimidine is reduced smoothly by the action of hydriodic acid giving 6-aminopyrimidine (XXVIII). Hydriodic acid cannot be used for the reduction of 2-mercaptochloropyrimidines because the mercapto radicle is destroyed by hydrolysis in the presence of this reagent.

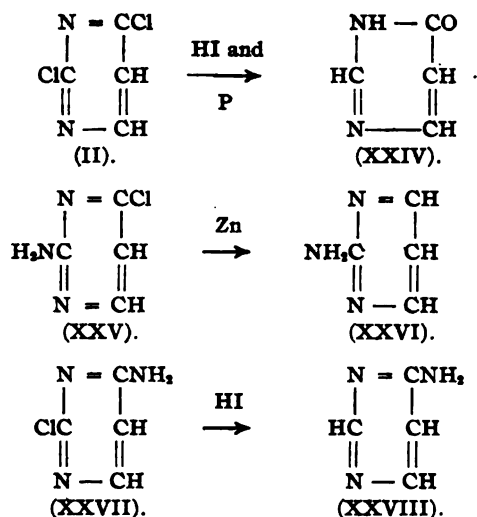
¹ Wheeler and Johnson, *Am. Chem. J.*, 29, 497 (1903); Wheeler and Bristol, *Ibid.*, 33, 450 (1905).

² Johns, *Am. Chem. J.*, 40, 351 (1908).

³ *Am. Chem. J.*, 38, 236 (1907).

⁴ *Ibid.*, 42, 355 (1909).

⁵ *J. Biol. Chem.*, 3, 289 (1907).



2-Mercaptopyrimidines can be obtained by condensation of 1,3-diketones with pseudothioureas. Wheeler¹ and Jamieson prepared, for example, 2-methylmercapto-4,6-dimethylpyrimidine (XXIX) by condensing ethylpseudothiourea with acetylacetone. The yield, however, was only 24.4% of the theoretical. It has been our experience that this method of synthesis is limited in its application. Many of the 1,3-diketones are extremely difficult to obtain in quantity and many of them, which we have examined, have failed to condense with pseudoureas. By reaction of the mercaptochlorides it should be possible to obtain new pyrimidine combinations which it would be practically impossible to synthesize easily by other known methods. Certain unknown representatives of this class of pyrimidines should be very valuable for further important synthesis.

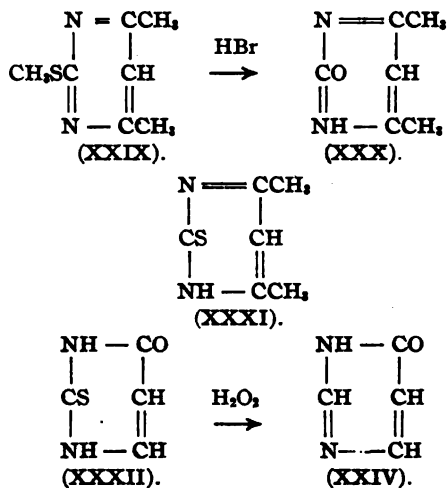
1,3-Diketones of the type of acetylacetone condense with urea and pseudourea giving the corresponding 2-keto- and 2-thiopyrimidines² (XXX and XXXI). Complications are, however, met with here unless special conditions are adopted, and a new method of synthesizing these types of compounds is desirable. It seems not improbable that their preparation from the 2-mercapto-1,3-diketones will prove to be a feasible method. Wheeler and Jamieson³ have shown that 2-methylmercapto-4,6-dimethylpyrimidine (XXIX) is convertible into 2-oxy-4,6-dimethylpyrimidine (XX), by hydrolysis with hydrobromic acid. We now find that the ethylmercapto-1,3-diketone represented by Formula XIX is transformed

¹ *Am. Chem. J.*, **32**, 356 (1904); Hale, *THIS JOURNAL*, **37**, 594 (1915).

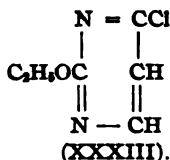
² Evans, *J. prakt. Chem.*, [2] **48**, 489 (1893); de Haen, *Rec. trav. chim.*, **27**, 162 (1908); Hale, *THIS JOURNAL*, **36**, 104 (1914); **37**, 594 (1915); **37**, 1544 (1915).

³ *Loc. cit.*

into the hitherto unknown 2-oxypyrimidine (XXII), by hydrolysis with hydrochloric and also hydrobromic acid. The isomeric 6-oxypyrimidine (XXIV) has been described by Wheeler¹ and was prepared by reduction of 2,6-dichloropyrimidine (II), with hydriodic acid, and also by the interaction of 2-thiouracil (XXXII) with hydrogen peroxide. Wheeler's ketone (XXIV) was a basic substance melting at 164–165°, and was characterized by its great solubility in water and alcohol. 2-Ketopyrimidine (XXII) is likewise a basic pyrimidine and forms stable salts with hydrochloric and hydrobromic acids. The free base, however, does not melt below 300° and is insoluble in water and the common organic reagents.



This investigation of 2-keto and 2-thiopyrimidines will be continued. We shall also continue our work on the reduction of mercaptopyrimidines, and their corresponding oxygen compounds, of which compound (XXXIII) is a typical representative.



Experimental Part.

2-Ethylmercapto-5-ethoxy-6-oxypyrimidine (VIII).—This mercaptopyrimidine, which was used in this investigation, was prepared by condensing ethyl α -ethoxy- β -hydroxylacrylate with pseudoethylthiourea according to the directions of Johnson and McCollum.¹

2,6-Dioxy-5-ethoxypyrimidine (IX).—This pyrimidine was formed smoothly by digesting 50 g. of the above mercaptopyrimidine with

¹ *Loc. cit.*

g. of chloroacetic acid (2 molecular proportions) in 200 cc. of water for 6 hours. Ethylmercaptan was evolved copiously with gradual solution of the mercaptopyrimidine. After the reaction was complete the aqueous solution was filtered quickly and cooled, when the dioxypyrimidine crystallized out. It melted at 275° with decomposition and the yield was 35 g. or 90% of the theoretical. This pyrimidine has previously been prepared by Johnson and McCollum¹ by hydrolyzing the mercaptopyrimidine with hydrochloric acid. Its formation, however, was not smooth under such conditions and the yield was small, due to the formation of the corresponding hydroxy compound—*isobarbituric acid*. None of the latter is formed when the hydrolysis is effected with chloroacetic acid.

2-Ethylmercapto-5-ethoxy-6-chloropyrimidine (XI) was prepared according to the directions of Johnson and McCollum¹ by the action of an excess of phosphorus oxychloride on the above mercaptopyrimidine. It was purified by distillation under diminished pressure and the yield was 85% of the theoretical.

2,6-Dichloro-5-ethoxypyrimidine (X).—Thirty-four grams of 2,6-dioxy-5-ethoxypyrimidine were placed in a distilling flask with 140 g. of phosphorus oxychloride and the mixture heated at $120-130^{\circ}$ for 3 hours. The resulting dark-colored liquid was then subjected to distillation under diminished pressure and the excess of phosphorus oxychloride removed by heating at 100° . The crude chloride was then poured upon crushed ice to destroy any phosphorus halide present and the pyrimidine extracted with ether. The yield was 37 g. or 90% of the theoretical. The melting point of this compound is 51° and not $41-2^{\circ}$ as previously recorded.² This pyrimidine is insoluble in water and is not decomposed by boiling water. If a strong acid is present (HCl) hydrolysis takes place at once and the dioxypyrimidine is formed.

Reaction Applied with 2-Ethylmercapto-5-ethoxy-6-chloropyrimidine (XI).—(1) *Action of Chloroacetic Acid:* This pyrimidine is not desulfurized smoothly by digestion with chloroacetic acid. Three grams of the pyrimidine were mixed with 3 g. of chloroacetic acid (2 molecular proportions) in 50 cc. of water and the mixture heated for several hours at $130-150^{\circ}$. No mercaptan was evolved and the liquid assumed a dark color indicating decomposition. On cooling, a black, viscous product was obtained, from which no definite compound could be isolated.

(2) *Reduction with Zinc Dust:* A mixture of 10 g. of the mercaptochloropyrimidine, 25 g. of zinc dust, 75 cc. of water and 75 cc. of 95% alcohol was boiled under a reflux condenser for 3 hours. Frequent agitation of the mixture is essential in order to prevent caking of the zinc on the bottom of the flask. When the reduction was complete the unchanged

¹ *Loc. cit.*

² Johnson and Guest, *loc. cit.*

zinc was separated by filtration and the excess of alcohol and water removed by heating at 100° under diminished pressure. A dark-colored oil separated. This was extracted with ether and the solution dried over calcium chloride (aqueous filtrate was saved). After removal of the solvent the pyrimidine was obtained as an oil which soon solidified. It was purified by crystallization from petroleum ether and separated in the form of thin, transparent plates or prisms, which melted at $31-32^{\circ}$ to a clear oil. The yield was 6.0 g. or 71% of the theoretical. The compound was identified as *2-ethylmercapto-5-ethoxypyrimidine* (XIV).

Calc. for $C_8H_{12}ON_2S$: N, 15.19 Found: N, 15.19, 15.10.

This pyrimidine is soluble in ether, benzene and alcohol and insoluble in water. The compound is a weak base, dissolving in acids and is reprecipitated by alkali. It forms a stable hydrochloride which easily undergoes hydrolysis in the presence of water. Molecular weight determination in benzene solution by the cryoscopic method:

Calc. for $C_8H_{12}ON_2S$: M. W., 184. Found: M. W., 180 and 182.

After the extraction of the above pyrimidine with ether, the aqueous filtrate was made strongly alkaline with concentrated sodium hydroxide solution. Sufficient alkali was added to dissolve the precipitated zinc hydroxide, when we obtained an insoluble, crystalline precipitate. This was separated by filtration, washed with water and finally crystallized from dilute alcohol. It separated from this solvent in the form of bunches of needles. The yield was 0.6 g. This compound, whose structure has not been established, was insoluble in alkali solutions and cold water and soluble in alcohol and hot water. It crystallized from dilute alcohol in beautiful needles which melted at $126-127^{\circ}$. Molecular weight determinations in benzene solution by the cryoscopic method gave the values 202 and 204. Whether we are dealing here with a stereoisomer of 2-ethylmercapto-5-ethoxypyrimidine or a different reduction product remains to be established.

Attempts were made to reduce 2-ethylmercapto-5-ethoxy-6-chloropyrimidine (XI) by digesting with zinc dust in the presence of boiling water, but under no condition could a smooth reduction be effected. The pyrimidine underwent partial decomposition with evolution of mercaptan and tarry products were formed with production of very poor yields of the reduced pyrimidine (XIV), melting at $31-32^{\circ}$.

Hydrochloride of 2-Ethylmercapto-5-ethoxypyrimidine.—This is easily prepared by saturating an ether solution of the pyrimidine with hydrochloric acid gas. It separated as stout prisms which melted at $120-121^{\circ}$.

Calc. for $C_8H_{12}ON_2S.HCl$: N, 12.69. Found: N, 12.64, 12.76.

Platinum Salt.—Prepared by adding chloroplatinic acid to a hydrochloric acid solution of the mercaptopyrimidine. It crystallized in golden-yellow prisms which melted at $165-166^{\circ}$.

Calc. for $(C_6H_7ON_2S)_2 \cdot H_2PtCl_6$: Pt, 24.86. Found: Pt, 25.09.

Action of Chloroacetic Acid on 2-Ethylmercapto-5-ethoxypyrimidine (XIV).—One gram of the mercaptopyrimidine and 1 g. of the halogenated acid were heated together in an oil bath for 10 hours. No mercaptan was evolved. One gram more of chloroacetic acid was added and the heating continued for 8 hours. Still no mercaptan was evolved. Water was then added and the solution extracted with ether. On evaporating the ether the unaltered mercaptopyrimidine melting at $31-32^\circ$ was recovered.

Digestion of 2-Ethylmercapto-5-ethoxypyrimidine with Zinc Dust.—One gram of the pyrimidine was digested in a mixture of 25 cc. of water and 25 cc. of alcohol with 1 g. of zinc dust for one hour. No further reduction was accomplished by this treatment and the unaltered pyrimidine was recovered.

Action of Alcoholic Ammonia on 2-Ethylmercapto-5-ethoxypyrimidine.—Two grams of the pyrimidine were sealed in a bomb tube with 30 cc. of strong alcoholic ammonia (saturated solution) and the mixture then heated at 100° for 24 hours. After cooling, and opening of the tube there was no odor of mercaptan. The tube was sealed again and heated for 10 hours at $130-150^\circ$. Under these conditions there was no reaction. The contents of the tube were again heated for 4 hours at $140-170^\circ$ and finally for 10 hours at $175-185^\circ$. After this vigorous treatment there was no formation of mercaptan and the pyrimidine was recovered unaltered.

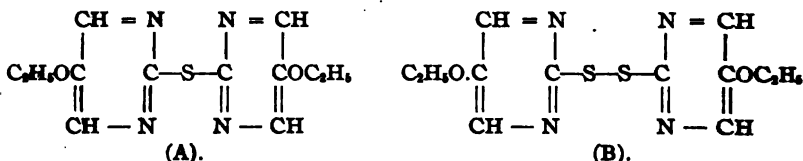
Reduction of 2,6-Dichloro-5-ethoxypyrimidine (X) with Zinc Dust: 2-Chloro-5-ethoxypyrimidine (XII).—Twenty grams of the dichloropyrimidine and 40 g. of zinc dust were suspended in a mixture of 100.0 cc. of alcohol and 100.0 cc. of water. This was then heated to boiling for 1.5 hours and the unchanged zinc separated by filtration. After removing the alcohol by heating under diminished pressure, the monochloropyrimidine separated in a crystalline condition. The yield was 13 g. or 80% of the theoretical. It was observed that the best results were always obtained by using a large excess of zinc dust and digesting for a limited period with equal parts of water and alcohol. A smaller proportion of zinc was tried, as was also longer boiling, but the yields of monochloropyrimidine were not so good. An attempt to reduce the dichloropyrimidine to its monochloro derivative by digestion with zinc dust and acetic acid was unsuccessful. This new pyrimidine is soluble in ether, alcohol and benzene and also in acids. It is insoluble in alkalis and in water. It can best be recrystallized from dilute alcohol and separates, on cooling, in thin, transparent plates, which melt at 70° to an oil. The compound possesses no odor, but is characterized by its peculiar effect when placed on the tongue. A cooling sensation is experienced and in small quantities it has a sweet taste.

Calc. for $C_6H_7ON_2Cl$: N, 17.66. Found: N, 17.65, 17.70.

Action of Potassium Hydrogen Sulfide on 2-Chloro-5-ethoxypyrimidine with Formation of 2-Thio-5-ethoxypyrimidine (XV).—Eight and four-tenths grams of potassium hydroxide were dissolved in 60 cc. of 95% alcohol and the solution thoroughly saturated with hydrogen sulfide. Six grams of the 2-chloropyrimidine were then dissolved in the solution and the mixture heated on the steam bath for 5 hours. It was then cooled and the potassium chloride separated by filtration. The solution was evaporated to dryness to remove the alcohol and the yellow residue acidified with dilute hydrochloric acid, when the 2-thio-5-ethoxypyrimidine (XV) separated as a bright, golden-yellow solid. It was purified by crystallization from about 20 parts of glacial acetic acid and separated in small yellow columns. They melted at 192–193°. The yield of crude material was 5 g. This pyrimidine is sparingly soluble in alcohol and benzene, insoluble in water, ether and acid solution (HCl). When digested with basic lead acetate solution, or mercury oxide suspended in water, metallic sulfides are formed. The pyrimidine dissolves in alkaline solutions and is reprecipitated by addition of acids.

Calc. for $C_8H_8ON_2S$: N, 17.95. Found: N, 17.85, 17.83.

After crystallization of this pyrimidine, the acetic acid filtrates were diluted with water, when a small amount of crystalline material separated. After crystallization from dilute alcohol this substance melted constant at 125°. It gave a strong test for sulfur. It was insoluble in both acid and alkalis, indicating one of the two sulfides below (A and B). Nitrogen



determinations agreed with the calculated value for the disulfide B.

Calc. for $C_{12}H_{14}O_2N_2S_2$: N, 17.90. Found: N, 17.87, 18.01.

Conversion of 2-Thio-5-ethoxypyrimidine into 2-Ethylmercapto-5-ethoxypyrimidine (XIV).—Two and five-tenths grams of the thiopyrimidine were converted into its potassium salt by dissolving the pyrimidine in 75 cc. of alcohol containing in solution 1 g. of potassium hydroxide. Fifteen grams of ethylbromide were then added and the heating continued for 3 hours. There was an immediate reaction with separation of potassium bromide. After filtering from potassium bromide, the alcohol was evaporated, when we obtained an oil, which was insoluble in water. It dissolved immediately in ether and on evaporation of the ether, deposited in long prisms melting at 31–32°. It was identified as the mercapto-pyrimidine which has been described in a previous experiment. A mix-

ture of the two substances melted at 31° . It formed a platinum salt which melted at $165-166^{\circ}$.

Action of Chloroacetic Acid on 2-Thio-5-ethoxypyrimidine, 5-Ethoxypyrimidine-2-thioglycollic Acid (XVI).—Two and eight-tenths grams of the thiopyrimidine were suspended in a solution of 2 g. of chloroacetic acid in 50 cc. of water. On boiling the solution the pyrimidine gradually dissolved and after heating for 5 hours the reaction was considered complete. There was no change of color. On cooling the acid solution, the thioglycollic acid separated in the form of needles. They were purified by crystallization from 95% alcohol and melted at $137-138^{\circ}$ to an oil. The yield was 2.5 g. The compound gave a strong test for sulfur and was soluble in alkaline but insoluble in acid solutions.

Calc. for $C_8H_{10}O_2N_2S$: N, 13.08. Found: N, 13.02, 13.3.

Attempts to Hydrolize the Thioglycollic Acid by Digesting with Hydrochloric Acid.—One and five-tenths grams of the thioglycollic acid were digested with hydrochloric acid (50 cc. concentrated acid) for 3.5 hours. The mixture assumed a dark, reddish brown color. The acid was removed by evaporation and the residue neutralized with sodium hydroxide to destroy any hydrochloride. After evaporating to dryness again, the residue was then extracted with alcohol and benzene, but nothing but tarry, indefinite products were obtained. The pyrimidine had apparently undergone complete decomposition.

The experiment was repeated using 10% hydrochloric acid. After boiling for 4 hours, the solution was evaporated under diminished pressure and the residue triturated with pure water. The unaltered pyrimidine was recovered in a crystalline condition. It crystallized from alcohol and melted at $137-138^{\circ}$.

2,5-Diethoxypyrimidine (XIII).—This pyrimidine was prepared by interaction of 2-chloro-5-ethoxypyrimidine, in alcohol, with the required amount of sodium ethylate. The reaction was rendered complete by heating for one hour on the steam bath. After filtering off the sodium chloride and evaporating the alcohol under diminished pressure at 40° , the pyrimidine was then extracted with ether and the solution dried over sodium sulfate. Calcium chloride could not be used because it formed a double combination with the pyrimidine. After removal of the ether we obtained 18 g. of the pyrimidine which boiled at 142° under a pressure of 24 mm. This compound crystallizes in beautiful, large, transparent plates, which melt at 19° . One of the crystals measured 1.375 inches on its longest axis and was 0.125 inch in thickness. The pyrimidine is insoluble in water and alkaline solutions but soluble in concentrated acids, ether, alcohol and benzene. It forms a hydrochloride which is easily hydrolized by moisture, and also forms an insoluble platinum salt.

Calc. for $C_8H_{12}O_2N_2$: N, 16.66. Found: N, 16.73, 16.50.

Hydrochloric Acid Salt.—This was prepared by saturating an ether solution of the base with hydrochloric acid gas. It separated in the form of colorless needles.

Calc. for $C_4H_5O_2N_2 \cdot HCl$: N, 13.69. Found: N, 13.81, 13.71.

Double Platinum Salt.—This crystallizes in golden-yellow prisms which melt at 176° with decomposition.

Calc. for $(C_4H_5O_2N_2)_2 \cdot H_2PtCl_6$: Pt, 26.16. Found: Pt, 26.12.

Reduction of 2-Ethylmercapto-6-chloropyrimidine (XVIII): 2-Ethylmercaptopyrimidine (XIX).—The chloropyrimidine was prepared according to directions already described in papers from this laboratory.¹ Our product boiled at $131-132^\circ$ under 20 mm. pressure and at 135° under 24 mm. The yield was 84% of the theoretical.

Fifteen grams of this chloride, together with 25 g. of zinc dust, were placed in a flask with 75 cc. of water and an equal volume of 95% alcohol. This mixture was then heated to boiling for one hour, the mixture being shaken occasionally to prevent caking of the zinc. During the reduction, the odor of mercaptan was noticeable. After the reduction was complete the zinc was separated by filtration and the filtrate evaporated under diminished pressure. A dark-colored oil separated as well as a small amount of crystalline material which proved to be uracil. The latter was separated by filtration and the oily 2-mercaptopyrimidine extracted with ether and its solution dried over calcium chloride. After removal of the ether the oil was purified by distillation under diminished pressure. It distilled at 115° at 20 mm. pressure. The oil was colorless and was characterized by its unpleasant, pungent odor. On exposure to the air it gradually assumed a dark color. The yield was 9 g. or 75% of the theoretical.

This pyrimidine does not solidify at 0° . It possesses basic properties and dissolves in concentrated acids. It is soluble in ether, alcohol and benzene, and is insoluble in water and alkaline solutions.

Calc. for $C_6H_8N_2S$: N, 20.00. Found: N, 19.93, 19.90.

Hydrochloride.—This was prepared by saturating an ether solution of the base with dry hydrochloric acid gas. The salt separated in colorless crystals and was dried, for analysis in a vacuum over sulfuric acid. It melted at $98-99^\circ$. The salt is unstable in damp air and dissociates into the free base and hydrochloric acid.

Calc. for $C_4H_5N_2S \cdot HCl$: N, 15.86. Found: N, 15.85, 15.87.

Double Platinum Salt.—This salt deposits as clusters of golden-yellow needles when chloroplatinic acid is added to a solution of the base in concentrated hydrochloric acid. It melts at 166° .

Calc. for $(C_4H_5N_2S)_2 \cdot H_2PtCl_6$: Pt, 28.27. Found: Pt, 28.22.

¹ Wheeler and Johnson, *Am. Chem. J.*, 29, 497; Wheeler and Bristol, *Ibid.*, 33, 450 (1905).

2-Oxypyrimidine (XXII).—Seven grams of the 2-mercaptopyrimidine were digested with 50 cc. of concentrated hydrochloric acid for 5.5 hours. The solution turned dark in color and ethylmercaptan was evolved. After the reaction was complete the solution was then evaporated to dryness, when we obtained a residue almost black in color, but crystalline in appearance. This was dissolved in water and the solution decolorized with bone-coal. The latter was then concentrated until crystals began to deposit when it was allowed to stand. The hydrochloride of the pyrimidine separated. This was purified by crystallization from 97% alcohol and melted at 203–205°.

Calc. for $C_4H_4ON_2.HCl$: N, 21.13. Found: N, 21.13.

The hydrobromide of the 2-oxypyrimidine was obtained by hydrolysis of the mercaptopyrimidine with hydrobromic acid. The hydrolysis, however, is not so smooth as when hydrochloric acid is used.

Calc. for $C_4H_4ON_2.HBr$: N, 15.82. Found: N, 15.77.

The free 2-oxypyrimidine can be prepared from its hydrochloride by dissolving the latter in water and exactly neutralizing the hydrochloric acid with dilute sodium hydroxide solution. Under these conditions the free pyrimidine separated as a light yellow, amorphous substance which did not melt at 320°. It possesses both acid and basic properties. It is sparingly soluble in water, alcohol, benzene and acetic acid, and practically insoluble in ether and ligroin. It is more soluble in a solution of ammonium chloride or ammonium bromide than in pure water.

2-Ethylmercapto-4-methylpyrimidine (XXIII).—The 2-ethylmercapto-4-methyl-6-chloropyrimidine (XXI), used in this experiment was prepared according to the directions of Johns.¹ Our product boiled at 142° under 15 mm. pressure. In order to convert this into the above pyrimidine, 25 g. of the chloride and 50 g. of zinc dust were suspended in a mixture of equal volumes of water and alcohol (100 cc.) and the mixture boiled for 2.5 hours. The excess of zinc was then separated by filtration and the solution evaporated at a temperature of 30–40° under diminished pressure. The pyrimidine separated as an oil, together with a little 4-methyluracil. The oil was dissolved in ether, dried over calcium chloride and finally distilled. It boiled at 123–124° at a pressure of 18–19 mm. It would not solidify at 0°. The yield was 15 g. or 72% of the theoretical. This compound has a pungent odor. It is a basic substance and is insoluble in alkalis. It is insoluble in water and soluble in ether, alcohol and benzene.

Calc. for $C_7H_{10}N_2S$: N, 18.17. Found: N, 18.05, 17.95.

Hydrochloride.—This crystallizes in prisms which melt at 141–142°. The salt is dissociated by water.

Calc. for $C_7H_{10}N_2S$: N, 14.70. Found: N, 14.71, 14.86.

¹ *Am. Chem. J.*, 40, 351 (1908).

Double Platinum Salt.—This crystallizes in needles which melt at 165–166°.

Calc. for $(C_7H_{10}N_2S)_2 \cdot H_2PtCl_6$: Pt, 27.17. Found: Pt, 27.14, 27.26.

A description of the products obtained by hydrolysis of this pyrimidine will be given in a future paper.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]
**STUDIES ON NITRATED PROTEINS. II. THE SYNTHESIS OF
3,5-DINITROTYROSINE.¹**

By TREAT B. JOHNSON AND EDWARD F. KOHMANN.

Received July 13, 1915.

In his paper entitled "Über das Tyrosin," Städeler² states that if special precautions are not taken in the preparation of *mono*-nitrotyrosine³ from tyrosine, and the proper proportions of nitric acid, water and tyrosine are not used, the nitrate of *mono*-nitrotyrosine will not separate from the acid solution. If such a condition develops and the resulting solution is allowed to stand and is then evaporated at a low temperature a new amino acid is obtained which crystallizes from boiling water in golden yellow plates. He concluded that this acid is *dinitrotyrosine*. The same amino acid is also obtained, according to him, by treatment of *mono*-nitrotyrosine with a mixture of equal parts of water and nitric acid (sp. gr. 1.3) at ordinary temperature, and then evaporating the acid solution at a low temperature. This transformation, however, was not quantitative because of the secondary formation of a large amount of oxalic acid and also a secondary nitrogenous substance which Städeler did not examine. According to this investigator the same dinitro compound is also formed by saturating tyrosine, suspended in water, with gaseous nitrous acid. Städeler described this amino acid as a yellow compound which crystallizes in plates that are difficultly soluble in cold and hot water, but easily soluble in alcohol and moderately soluble in ether. It possessed a sour taste and was characterized by the property of staining the skin, linen and other objects intensely yellow. No melting point was assigned to the compound, but Städeler states that at 100–115° it loses no weight, and when heated at a higher temperature decomposes with effervescence. He found by analysis 39.30% of carbon and 3.40% of hydrogen while the calculated values for these two elements are 39.85% and 3.32%, respectively. The percentage of nitrogen was not determined. Städeler

¹ Part of a dissertation presented by Mr. Edward F. Kohmann to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

² *Ann.*, 116, 82 (1860).

³ Johnson and Kohmann, *THIS JOURNAL*, 37, 1863 (1915).

described the potassium, barium, ammonium and lead salts of his acid which were all dark red in color.

The only other paper dealing with the chemistry of this amino acid, which has appeared since Städeler's work, is that published by Thudicum and Wanklyn¹ in 1869 under the title: "Researches on the Constitution and Reactions of Tyrosine." These investigators commented on the fact that Städeler did not determine nitrogen in his dinitrotyrosine and that his analytical results therefore did not exclude the possibility of there being O_3 in the place of an NO_2 group in the formula of his supposed dinitrotyrosine and called attention to the fact that his analytical results agreed quite as well with $C_9H_{10}(NO_2)NO_6$ as with $C_9H_9(NO_2)_2NO_3$. On repeating Städeler's work they failed in their attempts to make dinitrotyrosine and concluded from the peculiar results obtained that Städeler's dinitrotyrosine was probably nothing but an oxidized tyrosine. This, on prolonged oxidation, gave an abundant yield of oxalic acid. Thudicum and Wanklyn also made the interesting statement that there is no production of picric acid by oxidation of tyrosine with nitric acid. Furthermore, they were unable to verify Städeler's observation that tyrosine interacts with nitrous acid to form *dinitrotyrosine*. On the other hand, they obtained a highly colored combination whose structure was not established.

In connection with our investigations on nitrated proteins, it was necessary to determine under what conditions *dinitrotyrosine* is formed by the action of nitric acid on tyrosine, and also to establish definitely what positions in the benzene nucleus are occupied by the two nitro groups. Our first attempts to prepare the acid were unsuccessful, notwithstanding the fact that Städeler's directions were followed as closely as possible. In no case did we obtain evidence of its formation. If the nitric acid solution was allowed to evaporate spontaneously at ordinary temperature, or at higher temperatures, a mixture of oxalic acid and mononitrotyrosine was always obtained. Too energetic treatment led exclusively to the production of oxalic acid. In other words, nitrotyrosine was completely oxidized by vigorous treatment, and it consequently seems very doubtful whether dinitrotyrosine was actually obtained by Städeler.

We now find, that while the employment of nitric acid alone does not lead to the smooth formation of dinitrotyrosine, on the other hand, its synthesis can easily be accomplished by nitration of tyrosine with a mixture of concentrated nitric and sulfuric acids. Under proper conditions, which are discussed in detail in the experimental part of this paper, the acid can easily be obtained in excellent yields. Our amino acid differed, in its chemical behavior, in many ways from that described by Städeler. He states that his acid would not form a hydrochloride. Our acid, on

¹ J. Chem. Soc., 22, 283 (1869).

the other hand, forms smoothly such a salt. According to him dinitrotyrosine is soluble in alcohol and also ether, whereas our acid was found to be only very slightly soluble in alcohol and practically insoluble in ether. Our acid possessed no definite melting or decomposition point.

Städeler published analytical results agreeing with the calculated values for an anhydrous acid, and states that his product lost no weight when heated at 115°. We now find that dinitrotyrosine crystallizes with one molecule of water which is expelled from the acid by heating at about 140°. In the hydrated condition the acid is bright yellow in color, but when dehydrated assumes a bright red color. This is one of the most characteristic properties of this acid and serves for its identification. From the above data we are forced to conclude, therefore, that Städeler was dealing with some other substance, or, what seems most probable, impure mononitrotyrosine.

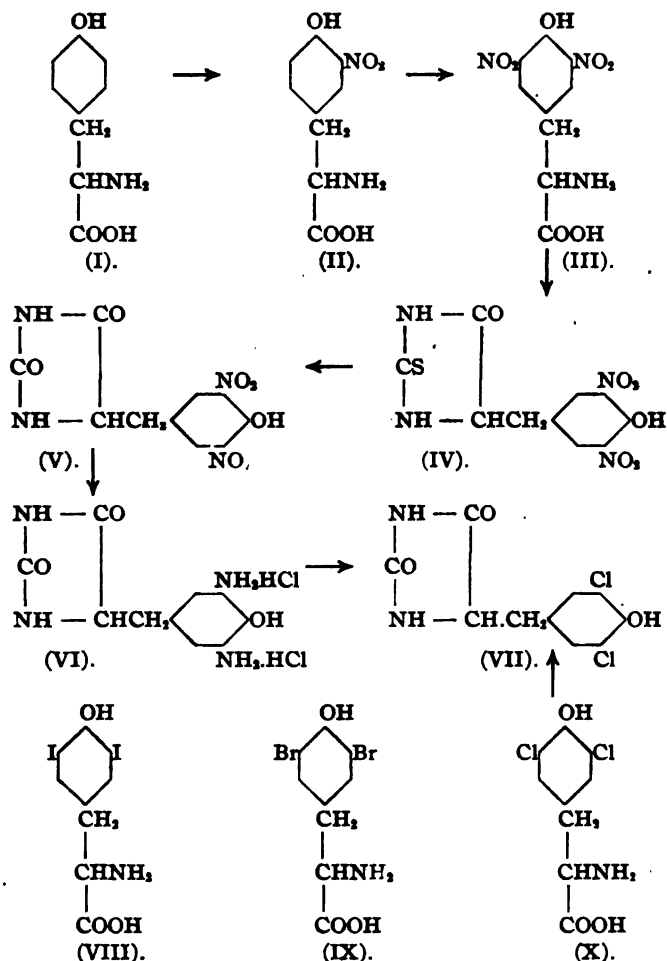
The constitution of our dinitrotyrosine was established in the following manner: The free amino acid was first condensed with ammonium thiocyanate in acetic anhydride solution according to the method of Johnson and Nicolet¹ and converted into the corresponding thiohydantoin represented by Formula IV. The latter compound, on digesting with an excess of 25% chloroacetic acid, was easily desulfurized and converted into the corresponding hydantoin (V). The yield was excellent. This dinitrohydantoin (V) was then reduced and converted into the hydrochloride of the diaminohydantoin represented by Formula VI. The latter, after diazotization, was then digested with cuprous chloride (Sandmeyer's reaction) and transformed into the corresponding dichlorohydantoin corresponding to Formula VII. This dichlorohydantoin proved to be identical in every respect with the hydantoin of 3,5-dichlorotyrosine, which has previously been described in a paper from this laboratory by Wheeler, Johnson and Hoffmann.² *Therefore, tyrosine, when it interacts with nitric acid in the presence of sulfuric acid, undergoes nitration with substitution in the two positions ortho to the hydroxyl group giving 3,5-dinitrotyrosine represented structurally by Formula III.*

These various changes are represented by the structural formulas below.

It is a well-known fact that *diortho*-substituted tyrosines like 3,5-diiodotyrosine (iodogorgoic acid) (VIII) and the corresponding dibromo- and dichloro-acids (IX and X) fail to give Millon's reaction. It was therefore, of especial interest to determine whether dinitrotyrosine (III) would conform to this behavior. We now find that it does not give the test. This observation is of interest and points to the conclusion that the production of the red color does not involve a nitration of tyrosine

¹ THIS JOURNAL, 33, 1973 (1911).

² J. Biol. Chem., 10, 147 (1912).



by the Millon reagent. The chemistry of this reaction will receive further attention in a later publication. In our first paper on nitrated proteins¹ attention was called to the fact that Loew examined the behavior of nitric acid and mixtures of nitric acid and sulfuric acids towards proteins. He made the observation that the proteins used failed to respond to Millon's test after such a treatment.² Moreover, it was noted that in one case mononitrotyrosine was obtained by hydrolysis of a nitrated protein (nitro-fibroin).³ Does this mean that when proteins are subjected to vigorous nitration that the tyrosine is converted largely into dinitrotyrosine? Furthermore, if it is formed, is it the precursor of picric

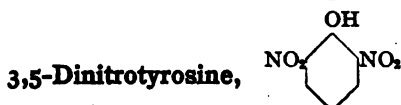
¹ Johnson and Kohmann, *loc. cit.*

² Loew, *J. prakt. Chem.*, [2] 3, 180.

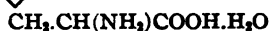
³ Inouye, *Zeit. physiol. Chem.*, 72, 486 (1911).

acid, which Welter¹ first obtained by vigorous treatment of the silk proteins with strong nitric acid? Our researches on nitrated proteins will be continued, and will include a study of polypeptide combinations of nitro- and dinitrotyrosine (II and III).

Experimental Part.



—After several pre-



liminary experiments the following procedure was finally adopted for the preparation of this interesting amino acid: First, an acid mixture is prepared by combining 22 g. of pure concentrated sulfuric acid and 3 g. of concentrated nitric acid. This mixture is then cooled to 10° and 2 g. of finely pulverized tyrosine added slowly in small portions while the solution was constantly stirred and the temperature kept below 10°. It is not advisable to nitrate more than 2 g. of tyrosine at a time and these should be added to the acid as rapidly as possible. A complete solution of the tyrosine is not effected by the operation and after final addition of the acid the mixture is then poured immediately into water. This operation was repeated six times and the combined solutions worked for dinitrotyrosine. In order to isolate the free acid, the sulfuric acid is exactly precipitated as barium sulfate and the barium free filtrate then made distinctly alkaline with ammonia and the resulting solution finally evaporated to dryness, by heating at 60° under diminished pressure. On treating the resulting residue with about 25 cc. of cold water the dinitrotyrosine is obtained in the form of a bright red ammonium salt moderately soluble in water. In order to obtain the free acid this salt is decomposed with a little dilute hydrochloric acid and the dinitrotyrosine dissolved in boiling water. It is well to digest with bone-coal here to clarify the solution. On cooling, the dinitrotyrosine crystallizes in beautiful, golden-yellow plates containing water of crystallization. From 12 g. of tyrosine we obtained 6 g. of pure dinitrotyrosine. Especially characteristic is the behavior of this acid when heated. When heated at 140–150° it loses its water of crystallization and assumes a brick-red color. At 220–230° it decomposes with effervescence. The acid does not lose its water of crystallization when heated at 110° as was shown by the following nitrogen determination:

Calc. for $\text{C}_8\text{H}_9\text{O}_7\text{N}_2\cdot\text{H}_2\text{O}$: N, 14.51. Found: N, 14.47.

When dried to constant weight at 150° the following results were obtained:

I. 0.4022 and 0.3714 g.; lost 0.0260 and 0.0237 g. H_2O .

Calc. for $\text{C}_8\text{H}_9\text{O}_7\text{N}_2\cdot\text{H}_2\text{O}$: H_2O , 6.23. Found: H_2O , 6.47, 6.38.

¹ *Ann. chim.*, 29, 301 (1796).

Nitrogen determinations in the anhydrous acid:

Calc. for $C_8H_5O_7N_3$: N, 15.50. Found: N, 15.45, 15.36.

The Behavior of Dinitrotyrosine towards Millon's Reagent.—This amino acid does not give a red color with Millon's reagent, but when boiled with the reagent is converted into a characteristic insoluble mercury salt. It can be prepared as follows: To a boiling Millon's solution is added an equal volume of a hot, saturated, aqueous solution of the amino acid when there immediately separates the yellow mercury salt. This is separated by filtration, washed with nitric acid and dried for analysis in the air. The salt is insoluble in the common solvents. It begins to decompose at 170° and effervesces at 185° . This salt was not examined further but will receive attention at a later period. It is not improbable that we may be able to develop a practical method for the quantitative separation of dinitrotyrosine from nitrotyrosine and tyrosine by application of this interesting reaction.

Calc. for $C_8H_5O_7N_3.HgNO_3$: N, 10.5. Found: N, 10.17, 10.22, 10.13.

The Hydrochloride of Dinitrotyrosine, $C_8H_5O_7N_3.HCl$.—This salt is prepared by dissolving dinitrotyrosine in hydrochloric acid and then adding to the solution strong hydrochloric acid. It separates in the form of bright yellow plates which begin to darken at 220° , when heated in a capillary tube, and decompose at 230° with effervescence. The salt dissolves in water and is precipitated by dilution with concentrated hydrochloric acid. The hydrochloride of *o*-nitrotyrosine is characterized by similar properties. For analysis, the salt was dried at 110° .

Calc. for $C_8H_5O_7N_3.HCl$: N, 13.60. Found: N, 13.51.

Ammonium Salt of Dinitrotyrosine.—This is prepared by dissolving the acid in a small volume of warm ammonia solution and then diluting this with strong aqueous ammonia. On allowing the solution to cool the salt finally deposits as beautiful, red prisms. The salt decomposed when heated above 230° . It was dried for analysis at 110° .

Calc. for $C_8H_5O_7N_3.NH_4$: N, 19.45. Found: N, 19.31, 19.25.

The Thiohydantoin of 3,5-Dinitrotyrosine (IV).—One and two-tenths grams of dinitrotyrosine, 0.6 g. of anhydrous ammonium thiocyanate and 5.7 cc. of acetic anhydride were warmed on a steam bath for one hour. A clear, orange-colored solution was obtained which was poured into an excess of cold water, when a dark-colored oil deposited, which soon solidified. This was separated by filtration, suspended in strong hydrochloric acid and the mixture finally evaporated to dryness to hydrolyze any 3-acetyl hydantoin present. The 2-thiohydantoin was left behind as a yellow powder. This was purified by crystallization from 50% acetic acid and separated in the form of burrs of short prisms. It melted at $225-230^\circ$ with decomposition. From 3.7 g. of dinitrotyrosine we obtained 4 g. of crude hydantoin.

Calc. for $C_{11}H_9O_5N_3S$: N, 17.93. Found: N, 17.91.

4-(3,5-Dinitro-4-hydroxybenzyl)-hydantoin (V).—This was prepared as follows: Four grams of the above thiohydantoin were desulfurized by digesting, in an oil bath at 140° , with 15 g. of chloroacetic acid and 45 cc. of water for 6 hours. A clear solution was obtained, from which on cooling, 2.9 g. of the hydantoin separated. This was purified for analysis by crystallization from glacial acetic acid and separated in large golden-yellow blocks, which decomposed at 235° . The hydantoin is insoluble in water.

Calc. for $C_{10}H_9O_7N_4$: N, 18.90. Found: N, 18.65, 18.85.

Formation of 4-(3,5-Dichloro-4-hydroxybenzyl)-hydantoin (VII) from 4-(3,5-Dinitro-4-hydroxybenzyl)-hydantoin (V).—Two grams of the hydantoin of 3,5-dinitrotyrosine were reduced by warming with 50 cc. of dilute hydrochloric acid and an excess of tin. After the reduction was complete the excess of acid was removed by evaporation, 400 cc. of water added to dissolve the residue and the tin finally precipitated with hydrogen sulfide. After separating from tin sulfide by filtration the filtrate was then concentrated to a volume of 10–15 cc. under diminished pressure and finally diluted with 10 cc. of concentrated hydrochloric acid. Two grams of sodium nitrate dissolved in 5 cc. of cold water, were then added slowly while keeping the solution cold. The corresponding diazonium salt separated as a yellow solid. After complete diazotization the mixture was then poured into 10 g. of strong cuprous chloride solution. On heating, nitrogen was evolved. After complete decomposition of the diazonium compound and cooling the solution, a crystalline substance separated. This contained chlorine and was identified as the hydantoin of 3,5-dichlorotyrosine. It was very soluble in alcohol and crystallized in rhombohedral prisms which melted at $202\text{--}203^\circ$. A mixture of this compound and a sample of the hydantoin of 3,5-dichlorotyrosine prepared by Wheeler, Johnson and Hoffmann¹ melted at the same temperature.

Calc. for $C_{10}H_7O_5N_2Cl_2$: N, 10.1. Found: N, 9.9.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]
**STUDIES ON NITRATED PROTEINS. III. THE CONVERSION
 OF FIBROIN INTO NITRO-FIBROIN (FIBROIN-XANTHO-
 PROTEIC ACID).**

BY TREAT B. JOHNSON, ARTHUR J. HILL AND LEON P. O'HARA.

Received July 3, 1915.

In our study of the chemistry of the xanthoproteic reaction for proteins, it was apparent to us, after considering what had already been done by previous investigators and also from what we learned by making

¹ *Loc. cit.*

several preliminary tests on our part, that the success of any research dealing with the action of nitric acid on proteins depended to a large extent on the selection of the proper protein material for investigation. It was necessary that the latter be easily obtainable in a high state of purity and be composed of a small number of the characteristic protein α -amino acids. After considering several proteins of both animal and plant origin, we decided that no representative of this class of natural substances, which was available in quantity, fulfilled so well the essential conditions as the characteristic protein—*fibroin*. This can be obtained extremely pure without apparent alteration of its molecular structure, and practically constant in composition. According to the best analyses about 70% of the molecule of fibroin from Italian silk is composed of the three α -amino acids, namely, glycocoll, alanine and tyrosine, which are present in the proportions of 36, 21 and 10%, respectively. This protein is practically free from histidine, and the presence of arginine has been detected by only two investigators.¹ They obtained by hydrolysis of a purified fibroin about 1.0% of its weight in this amino acid. Fibroin contains a small percentage of aspartic acid and in only one case has it been shown that glutaminic acid is present in greater proportion than 3.5% of the molecule.² Canton and Italian silk fibroin contain only 1.6 and 1.25%, respectively, of phenylalanine. Fibroin does not contain tryptophane.

It is well known that silk fibroin is colored strongly yellow by the action of strong nitric acid, and by vigorous treatment with the concentrated acid is completely destroyed with the production of picric acid.³ By some investigators the production of the yellow color is assumed to be due to the formation of xanthoproteic acid,⁴ while others believe that picric acid in the reagent involved, which then dyes the silk yellow. The action is undoubtedly a very peculiar one and regarding the real nature of the first phases of the reaction we have very little knowledge. It remains to be established whether the reaction between a protein and nitric acid can be so regulated as to lead to a nitro protein possessing chemical individuality.

The behavior of nitric acid towards silk was investigated as early as 1859 by Vogel.⁵ This investigator used apparently crude ungummed material and obtained by action of nitric acid and by a subsequent treatment with ammonia a yellow substance to which he assigned the formula

¹ Fischer and Skita, *Z. physiol. Chem.*, 35, 221 (1902).

² Fischer, *Z. physiol. Chem.*, 53, 126 (1907).

³ See our first paper by Johnson and Kohmann, *THIS JOURNAL*, 37, 1863 (1915).

⁴ Mulder, *Ann.*, 28, 73 (1838).

⁵ *Buchner's neues Repert*, 8, 1; *Handwörterbuch der reinen u. angew. Chem.*, 7, 743 (1859).

$C_{48}H_{36}O_9N_6$. He states that different substances are obtained according to the length of time of action of the acid on the protein.

Vignon and Sisley¹ investigated in 1891 the behavior of silk fibroin towards both nitric and nitrous acids. Nitric acid of density 1.33 was used and the observation made that the protein was colored intensely yellow. This was fast to light and was intensified by treatment of the fibroin with alkaline solutions. They made the observation that nitrous acid probably functionates in this change and observed that nitric acid free from nitrous acid will not produce the yellow color. When they reversed their process and treated silk first with nitrous acid a yellow color was also produced, but it was not fast to light. However, if the protein was afterwards treated with nitric acid the yellow color was rendered permanent. Their method of treatment led to an increase of 2% in the weight of the silk and they found 21.6% of nitrogen in their nitrated protein while the original fibroin contained 18.8%. The differences between fibroin and Vignon and Sisley's nitrated protein are recorded in Table I.

TABLE I.

Reagent.	Fibroin.	Nitrated protein.
Conc. H_2SO_4	Soluble giving a colorless solution	Swells up and gives a transparent, viscous mass like albumen
Strong caustic potash	No reaction in cold. On warming dissolves with evolution of ammonia	Turns red and dissolves on warming with evolution of ammonia
Conc. HCl	Soluble	Soluble
$ZnCl_2$ solution	Soluble	Soluble
Dry distillation	Carbonizes with evolution of ammonia	Burns without deflagration. Burns more rapidly than fibroin

This work of Vignon and Sisley² was followed by that of Inouye³ in 1912, who prepared a nitro-fibroin by nitration of fibroin, and investigated the character of the nitroamino acids formed by its hydrolysis with sulfuric acid.

In our work, the results of which are described in this paper, we have confined ourselves to a study of the behavior of fibroin towards nitric acid of specific gravity 1.12. The temperature has been kept uniform (18–25°) and the time period has been carefully regulated. The change in the protein has been studied quantitatively as well as qualitatively. After carrying out, under specific conditions, a series of nitration experi-

¹ *Bull. soc. chim.*, [3] 6, 898 (1891); *Ber.*, 25, R. 14 (1892); *Compt. rend.*, 113, 701 (1891).

² *Loc. cit.*

³ *Z. physiol. Chem.*, 81, 80 (1912).

ments on pure fibroin, we have made the interesting observation that the action of the acid on the protein is a gradual process until about 30% of the fibroin is carried into solution. This condition obtains after exposure to the action of the acid for about 192 hours. The remaining 70% of the original fibroin is left behind, suspended in the acid, as a pulverulent, orange-colored powder which is very resistant to further action of the acid. This modified protein, the properties of which are described in the experimental part of this paper, remained practically unchanged after submersion in nitric acid of sp. gr. 1.12 for thirteen days. It is questionable whether our nitrated product is identical with the so-called nitrofibroin described by Inouye.¹ Before this can be established it will be necessary to develop methods of determining quantitatively the relative proportions of the characteristic, hydrolytic products containing nitro groups. (This work is now in progress.)

Inouye's product was obtained after 48 hours' treatment with nitric acid and he states that his yield was equivalent to 85-90% of the weight of silk taken. We now know that the action of nitric acid (sp. gr. 1.12) on fibroin is not complete at the end of this period.

So far as the action of nitric acid is concerned the behavior of our final product conforms to that of an organic combination of definite constitution. Whether a nitric acid weaker than that used will lead to the formation of the same combination by longer treatment remains to be established. There are undoubtedly side reactions involved which can be regulated by choosing an acid of the proper strength.

It is an interesting fact that the nitration reaction can be followed qualitatively by Millon's test for only a few hours. After 24 hours' treatment the nitrated protein failed to respond to the test. This would indicate that the reaction was complete, but it was on observation that the reaction continued beyond this stage. Whether this indicates that the tyrosine nucleus of the protein (fibroin) is completely converted after 24 hours into a dinitro combination will be determined by a careful study of the products of hydrolysis. Our new hydantoin derivatives, which we have described in previous papers, should prove of great value² for the isolation and identification of the nitro combinations formed. This work is now in progress.

Experimental Part.

Preparation of the Silk for Nitration.—The protein (fibroin) that was used in our work was a very fine grade of silk-wools, which was furnished to us gratuitously by the manufacturer.³ The wools were of excellent quality and exceptionally free from foreign material (dirt). Al-

¹ *Loc. cit.*

² Johnson and Kohmann, *Loc. cit.*

³ The Cheney Brothers, silk manufacturers, South Manchester, Connecticut.

though the material used was a thoroughly degummed product, care was taken, however, to carefully cleanse it of any adhering fatty material previous to nitration. The cleansing procedure was as follows: One pound of silk-noils was boiled with 15 liters of a neutral 1.0% red-oil soap solution for a period of six hours. The silk was then thoroughly washed with warm and cold water to remove the soap solution and finally desiccated at a constant temperature of 100°. This material was then preserved in a desiccator over sulfuric acid and used as needed.

Physical Condition of the Silk.—It has been our experience in conducting nitration experiments on silk fibroin that the results obtained are dependent, to a great extent, upon the physical nature of the fibre. In order to obtain consistent results under a given set of conditions, it is necessary that the natural condition of the fibre, as obtained after the degumming process, be preserved as much as possible. If pure spun silk in skein form or a silk yarn of close texture is used for experimental purposes, entirely different results will be obtained, under prescribed conditions, than when silk-noils are used. In the case of skein silk the individual fibres are closely packed and when the silk is moistened with acid there is a tendency for the fibres to swell, thus producing a very close texture. With such material the action of the acid is superficial and it takes a much longer treatment to obtain a uniform nitrated product. On the other hand, when silk-noils are used the action of the acid is quicker and also more uniform. The silk fibres in this material are very short and more porous, due to the mechanical treatment to which the silk has been subjected. Consequently, a greater surface is offered for the action of the acid. The action is not superficial and a stirring process can be successfully applied during the nitration which enables one to effect thorough incorporation of the acid into the fibre.

Nitration of the Fibroin.—The nitration experiments were carried out in tall, slender, cylindrical beakers of 1200 cc. capacity. Twenty grams of the dried noils were carefully weighed into the latter for each experiment and then covered with 1000 cc. of an aqueous solution of nitric acid (sp. gr. 1.12). The purest, concentrated nitric acid was used. The beakers were covered with watch glasses and the nitration allowed to proceed at the temperature of the laboratory (18–25°), with frequent stirring of the silk suspension in order to have a uniform action. At the end of the given nitration period the nitrated product was filtered by suction and then washed repeatedly by maceration with cold water until the wash liquor gave no acid reaction. The nitrated protein was then dried at 100° and weighed to determine the yield. The nitrogen content of the nitrated product was estimated by the Kjeldahl method modified to include the nitrogen of nitrates. Salicylic acid was used in every digestion.

TABLE II.—YIELDS OF NITROFIBROIN AND CORRESPONDING NITROGEN PERCENTAGES.

	Amount of silk used. Grams.	Specific grav. of HNO_3 used.	Time period of nitration. Hours.	Dehydration temperature.	Amount of acid used. Cc.	Yield of nitrated silk.	Nitrogen content of nitrated silk.	
							(a).	(b).
1.....	20	1.12	12	100°	1000	19.9608	17.92	17.90
2.....	20	1.12	18	100°	1000	19.4584	18.12	18.17
3.....	20	1.12	24	100°	1000	18.7224	18.34	18.29
4.....	20	1.12	48	100°	1000	17.5459	18.77	18.76
5.....	20	1.12	72	100°	1000	17.2848	17.78	17.78
6.....	20	1.12	96	100°	1000	16.4710	17.82	17.70
7.....	20	1.12	120	100°	1000	16.3221	17.84	17.65
8.....	20	1.12	144	100°	1000	16.1102	17.76	17.75
9.....	20	1.12	168	100°	1000	15.3647	18.03	18.12
10.....	20	1.12	192	100°	1000	14.3452	18.08	18.08
11.....	20	1.12	216	100°	1000	14.2902	18.02	18.01
12.....	20	1.12	240	100°	1000	14.2402	18.12	18.05
13.....	467.5	1.12	240	100°	23,730	33.350	18.00	18.01
14 ¹	20	1.12	240	100°	1000	14.2670	18.00	18.01
15 ¹	20	1.12	552	100°	1000	12.0000	18.10	18.05

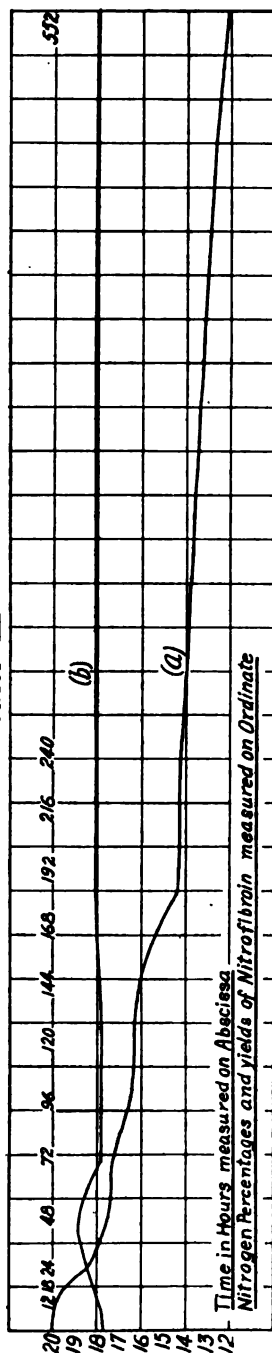
Following in every detail such a procedure as described above, a series of nineteen experiments were carried through differing from each other only as regards the length of time of nitration, which ranged from 12 to 552 hours. The various yields of nitrofibroin obtained from these different experiments, together with the corresponding nitrogen contents in percentages, are recorded in Table II. Both the percentages of nitrogen found and the respective yields of the several experiments have been expressed graphically in Table III by the Curves *a* (yields of nitrofibroin) and *b* (percentages of nitrogen found). Divisions of time, expressed in hours, have been plotted on the abscissa and the percentages of nitrogen and yields of nitrofibroin on the ordinate. Curve *a* commences on the ordinate at 20, the amount of fibroin taken for each experiment. Its nitrogen content (of the fibroin) is the intersection of *b* with the ordinate at 17.74. Curve *a* falls steadily below 20 finally intercepting curve *b* at 28 hours, and remaining below it from that point on.

No decisive conclusions can be drawn from inspection of the two curves below the 72-hour period. After this period *b* shows a constant valuation, while *a* constantly falls until the 192-hour period, when it then runs nearly parallel to curve *b* for the remaining 240 hours. This parallelism points to the interesting fact that we are dealing here with a definite product of nitration. The chemical deportment of our product was in accord with such an assumption. When our nitrofibroin, which we obtained by treatment of fibroin with nitric acid for 240 hours, was allowed to stand in freshly prepared nitric acid (sp. gr. 1.12) for a second period of

¹ 14 is 131 calculated on the basis of 20 g. silk, instead of 467.5 g.

² At the end of 240 hrs. treatment, the suspension was filtered and then immersed in a fresh quantity of 1000 cc. of HNO_3 (1.12).

Table III



13 days at ordinary temperature only a comparatively small loss of weight was incurred. It was no more than what would be expected from a slight solubility of the product in the acid. Furthermore the content of nitrogen remained constant at 18%. In order to substantiate further the conclusion that our treatment of fibroin with nitric acid of specific gravity 1.12, at ordinary temperature, is productive of a definite nitrated product which is very resistant to further action of the acid, a nitration experiment was carried through on a much larger unit. 467.5 g. fibroin were subjected to the action of the nitric acid (using the usual proportion as given in Table I) for 240 hours. After washing free from nitric acid and drying at 100° we obtained 333.5 g. of the nitrated protein, which gave on analysis (Kjeldahl) exactly 18% of nitrogen. In other words, the yield of nitrofibroin was exactly proportional to that obtained when only 20 g. of fibroin were nitrated.

$$467.5 : 333.5 :: 20 : 14.267.$$

On inspection of Table II, it will be seen that we actually obtained in the 216 and 240 hours' experiments with 20 g. of fibroin the values—14.2902 and 14.2670 g., respectively.

Description of the Nitration Experiments.—

The behavior of the noils, after submersion in the nitric acid, was followed very closely. At first there was no apparent action. After 15 minutes the first evidence of nitration was generally noticed. The action, however, was local and at first the silk became yellow in spots which rapidly diffused through the individual fibres as the action was continued. At the end of 12 hours the entire mass generally assumed a light, golden-yellow color of even distribution. After 12 hours' treatment the silk fibres were coherent in appearance, and, in fact, did not lose their identity until after several hours' longer treatment. After 96 hours, disintegration of the fibres was

seen to commence. The material had then assumed a deep, golden-yellow color and the protein, after drying, could easily be pulverized by rubbing in the hand. Further nitration produced nothing but a powder of nitrated protein. The final products obtained after nitration for 240 and 552 hours, respectively, consisted of deep, golden-yellow, pulverulent material which resembled very much mosaic gold in its physical characteristics. It did not possess a crystalline structure.

The progress of the nitration reaction was followed by application of the Millon's test for tyrosine. Samples of nitrated silk obtained from 0 to 44 hours' treatment with the nitric acid (sp. gr. 1.12) responded positively to the test. The intensity of the color, however, continually decreased by prolonged treatment and at the end of 24 hours the protein gave only a very slight coloration. None of the nitrated products obtained after treatment of the silk for 24-552 hours responded to the Millon reaction. The acid filtrates from these were also examined but in no case was a positive tyrosine test obtained.

TABLE IV.—ACTION OF MILLON'S REAGENT ON NITRATED FIBROIN.

Time in hours.	Nitrated protein.		Acid filtrates.	
	Warm Millon's reagent.	Bolling sol.	Warm Millon's reagent.	Bolling sol.
0	Deep red	Deep red
12	Faint red	Faint red
18	Slight red color	Slight red color
24	Slight red color	Slight red color
25 to 552	No Millon's test given in any case			

Properties of the Nitrofibroin.—Table V exhibits the principal differences between fibroin and our nitrofibroin.

TABLE V.

Reagent.	Fibroin.	Nitrofibroin.
Millon's sol.	Red color	No red color
Aqueous ammonia	Insoluble	Insoluble
Alkaline carbonates (in water)	Insoluble	Insoluble
1% caustic soda solution	Insoluble	Insoluble
Strong caustic soda solution	Soluble (hot) and is reprecipitated by dilution with water	Insoluble in 10% solution. Color changes from yellow to red which becomes more intense on heating. Alkaline solution takes on a light orange color and is decolorized on making acid. No precipitate is produced Insoluble in 50% sodium hydroxide solution. Solution, however, is colored orange. This color disappears at neutral point or when solution is made slightly acid

TABLE V (continued).

Reagent.	Fibroin.	Nitrofibroin.
Glacial acetic acid	Soluble in hot solution	Insoluble
Conc. HCl	Soluble	Soluble
Conc. H ₂ SO ₄	Soluble	Soluble
Conc. HNO ₃	Soluble	Soluble
Application of heat (Melting point)	Disintegrates at about 170°. No definite decomposition point	Begins to turn brown at about 240° and at 300° is almost black. No definite decomposition point
Copper oxide in am- moniacal solution (Schweitzer's re- agent)	Soluble in hot solution	Insoluble
Nickel oxide in am- moniacal solution	Soluble in hot solution	Insoluble
Biuret reaction	Positive	Color does not develop on account of orange color of the alkaline solution
Strong KOH solution (50%)	Soluble with evolution of ammonia	Soluble in hot solution with slight evolution of ammonia

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

THE SEPARATION OF MONO- β -, 2,6- AND 2,7-SULFONIC ACIDS OF ANTHRAQUINONE.

By M. L. CROSSLEY.

Received July 9, 1915.

Mono- β -, 2,6- and 2,7-sulfonic acids of anthraquinone, the products of direct sulfonation, are said to be easily separated as calcium salts which ultimately can be converted into the acids.¹ In preparing these acids I have observed that when the lime treatment is used a considerable portion of the calcium salts of mono- β - and 2,6-acid is thrown out of solution and discarded with the calcium sulfate. As a result a poor yield of the acids is obtained. Especially is this true when the sulfonation is intended to give the 2,6- and 2,7-acids as the chief products.

After considerable experimentation with different methods, I find that the best yields are obtained on separating the acids as their sodium salts by the direct neutralization of the sulfonated mixture with sodium hydroxide. By careful concentration of the solution of sodium sulfonate the mono- β - and 2,6-salts can be separated together, leaving the bulk of the sodium sulfate in the filtrate with the 2,7-salt, from which it can be precipitated by ethyl alcohol. The first two salts are separated from each other by their different solubilities in water. In addition to the three salts already mentioned, I have obtained a new substance which has not previously been described.

¹ Beilstein's *Handbuch der Organische Chemie*, 2, 406.

50 g. of best anthraquinone, recrystallized from benzene, and 18 g. of concentrated H_2SO_4 were mixed to a uniform paste in a casserole, 82 g. of fuming H_2SO_4 (60% SO_3) were then added. The casserole was covered with a watch glass and heated in an oil bath to 170° (thermometer in the oil) for two hours. A dark red pasty product was obtained. This was poured carefully into a liter of water and the mixture boiled for half an hour. It was then filtered while hot to remove unchanged anthraquinone. The filtrate was treated with a concentrated solution of sodium hydroxide until almost neutral and then evaporated to a thick paste. This was filtered and then pumped free of liquid. The solid was a mixture of mono- β - and 2,6-sodium sulfonates. These were separated from each other by their different solubilities in water and recognized by their sulfone chlorides, amides, and esters. The 2,6-sodium sulfonate is extremely sensitive to sunlight and changes from a light plum color to almost black.

The dark ruby-red filtrate from the pasty mixture was treated with 95% ethyl alcohol until no further precipitate of sodium sulfate formed. This was filtered and the filtrate evaporated over a water bath almost to dryness. The residue was then taken up in a very small amount of distilled water and to this solution was added a large excess of 95% ethyl alcohol, whereupon, a salmon-pink substance separated. This has very striking properties and is different from any of the anthraquinone derivatives thus far studied. It was filtered and dried at 150° . It dissolves readily in distilled water, giving a golden-yellow solution which changes to pink on adding a small amount of tap water.¹ This color change is not permanent and when the pink solution is exposed to sunlight for about twenty-four hours it completely changes back to the original golden-yellow color. The pink color can be again developed by the addition of tap water. If the exposure to sunlight is continued for two or three days no amount of tap water will re-establish the pink color. If a drop of dilute sodium hydroxide is added to the pink solution and it is then exposed to sunlight, the pink color is not discharged but instead it darkens to permanent ruby-red. The substance behaves as a very sensitive indicator, being reddish pink in alkaline solution and golden-yellow in acid solution. The pink color is not discharged by carbon dioxide. The compound is practically insoluble in acetone, acetic acid, benzene, ethyl alcohol, ether, ethyl acetate, aniline, ligroin, nitrobenzene, and pyridine. It is slightly soluble in methyl alcohol. Chloroform changes it to a dark red oil which is not soluble in an excess of the solvent. On standing this oil solidifies to a mass of beautiful red needle-shaped crystals. It also forms a dark red oil with toluene and this solidifies to a mass of rod-

¹ The tap water referred to was the City of Providence water and also Middletown water.

shaped crystals. When the substance, suspended in 95% ethyl alcohol, is exposed to sunlight, it changes to a beautiful dark green compound. This, when filtered and dried, slowly reverts back to the original salmon-pink substance. The transformation takes place very slowly when the substance is protected from sunlight. The change, however, is sufficiently rapid to prevent accurate information being accumulated with regard to the exact composition of the green compound. I have not felt certain that any one of the analyses of this substance represented a compound of uniform composition. No concordant results have been obtained. It appears to be a loose addition product of the salmon-pink compound. I reserve judgment in regard to the constitution of these substances until some later date when more evidence has been established from the continuation of the work in this laboratory.

The alcohol filtrate from the salmon-pink compound was again evaporated to dryness and the residue taken up in distilled water. To the solution was added about ten times its volume of 95% ethyl alcohol. There was no precipitate formed. The alcohol solution was evaporated to dryness and the residue shown to be 2,7-sodium sulfonate.

Yields: Mono- β -sodium sulfonate, 2 grams; 2,6-sodium sulfonate, 60 grams; 2,7-sodium sulfonate, 28 grams; new substance, 9 grams.

By the calcium treatment only 40 g. of 2,6 were obtained. None of the new substance was isolated. The yield of 2,7 averaged 29 g. and only a trace of mono- β or "silver salt" was obtained.

In order to produce the "silver salt" as the chief product of the reaction, 50 g. of best¹ anthraquinone and 9 g. of concentrated sulfuric acid were mixed to a uniform paste, to which were then added 41 g. of fuming sulfuric acid (60% SO_3). The reaction was carried out in a casserole. This was covered with a watch glass and heated in an oil-bath to 160° for two hours. The sulfonated product was then poured into water and boiled for half an hour. It was then filtered to remove the unchanged anthraquinone. The filtrate was treated with sodium hydroxide until almost neutral and then evaporated over a water bath to about one-third of its volume. On cooling, the mono- β -sodium sulfonate or silver salt separated. It was filtered and dried. The average yield obtained in this way was 38 g. The calcium treatment by the same method of sulfonation only yielded an average of 29 g. In the course of this work it was found that the "silver salt" separates best in mildly acid solution.

Summary.

The mono- β -, 2,6- and 2,7-sulfonic acids of anthraquinone are most advantageously separated as sodium salts by the direct neutralization

¹ Merck's.

of the sulfonic acid mixture with sodium hydroxide and the subsequent separation of these by their different solubilities in water.

On neutralization of the sulfonated mixture with lime much of the calcium salts of mono- β and 2,6 is lost in the calcium sulphate.

2,6-Sodium sulfonate of anthraquinone is very sensitive to sunlight, darkening in color from plum to almost black.

A new substance has been isolated. It has some interesting properties. When suspended in ethyl alcohol and exposed to sunlight an unstable green product results.

"Silver salt" separates best in mildly acid solution.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE NEUTRAL AMMONIUM SALTS OF SOME SUBSTITUTED BENZOIC ACIDS.

[FIFTH COMMUNICATION.¹]

BY LEROY MCMASTER AND I. H. GODLOVE.

Received June 29, 1915.

This work is a continuation of the preparation and investigation of the properties of the neutral ammonium salts of organic acids. This paper deals with the derivatives of benzoic acid. The salts described in the previous papers were prepared by passing dry ammonia into solutions of the organic acids in methyl alcohol, ethyl alcohol, ether, and acetone, or in mixtures of these solvents.

In the following work the neutral ammonium salts of *m*-toluic, *p*-toluic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, *o*-bromobenzoic, *m*-bromobenzoic, *p*-bromobenzoic, *o*-nitrobenzoic, *m*-nitrobenzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic, *o*-aminobenzoic, *m*-aminobenzoic, and *p*-aminobenzoic acids have been prepared by passing dry ammonia into solutions of the respective acids in the above anhydrous solvents, and some of their properties studied. After the salts were precipitated and tested for neutrality, they were filtered by suction on an alundum crucible and thoroughly washed with anhydrous ether. They were then put into crystallizing dishes and allowed to stand a short time in a vacuum desiccator.

Several of the salts were also prepared in pure benzene. Currie² states that the ammonium salts of weak organic acids can be prepared by passing dry ammonia into a benzene solution of the acids, and in this manner prepared the ammonium salts of caproic, caprylic and capric acids.

¹ For previous papers on this subject see: *Am. Chem. J.*, 49, 84-7 (1913); *Chem. News*, 108, 136-7 (1913); *Am. Chem. J.*, 49, 294-301 (1913); *Chem. News*, 108, 182-3, 193-4 (1913); *THIS JOURNAL*, 36, 742-7 (1914); *Chem. News*, 110, 212-4 (1914); *THIS JOURNAL*, 36, 1916-25 (1914); *Chem. News*, 110, 224-8 (1914).

² *J. Agr. Research*, 2, 8 (1914).

The analysis of the salts consisted in determining the nitrogen by either the regular or a modified Kjeldahl method. In all the salts, except those of the three amino acids, the nitrogen present as "ammonium" nitrogen was determined. This is equal to the total nitrogen, except for the nitro acids. For the three amino acids, total nitrogen was determined. In the case of the *m*-nitro acid, both total and ammonium nitrogen were determined.

The Toluic Acids.

Ammonium *m*-Toluate.—No record can be found of the preparation and properties of this salt. It was prepared by passing dry ammonia gas into an ether solution of *m*-toluic acid. On passing in the gas, there was first formed an amorphous powder which, after a time, became crystalline. The powder, after being filtered, washed with ether and dried, was dissolved in ethyl alcohol, from which it recrystallized in the form of long prismatic needles. It crystallizes from acetone in the same form. It is readily soluble in water, to which it imparts a neutral reaction. It is easily soluble in methyl alcohol, ethyl alcohol and acetic acid. It is also soluble in acetone but a little less so than in the last named solvents. The salt is somewhat hygroscopic, and gives off ammonia in the air. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.19% N.

Ammonium *p*-Toluate.—Noad¹ prepared this salt by neutralizing an aqueous solution of the acid and allowing the solution to evaporate. The salt crystallized out in the form of small prisms. No analysis was made of the salt. Lossen² found that the neutral salt could be prepared, in the form of clear, flat cubes, by cautious evaporation of a solution of the acid in ammonia water. He also obtained it in glittering leafy crystals, upon the addition of an excess of alcoholic ammonia to an alcoholic solution of the acid. If an aqueous solution of this salt were boiled and the solution allowed to cool, needle-shaped crystals of the acid salt were obtained, which crystallized from alcohol in the form of large silvery white glistening leaves.

We prepared this salt by passing dry ammonia into an ether solution of *p*-toluic acid. It precipitated as a fine, white, crystalline powder, which formed small needles when recrystallized from alcohol. The salt is soluble in water, methyl alcohol, ethyl alcohol, acetone and acetic acid. It is insoluble in ether. The aqueous solution of the salt is at first neutral, but slowly becomes acid, due to hydrolysis. The salt is only slightly hygroscopic, and gives off ammonia slowly in moist air.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.06 and 9.11% N.

¹ *Ann.*, 63, 296 (1847).

² *Ibid.*, 298, 72 (1897).

The neutral ammonium salt of *o*-toluic acid has been previously prepared by one of us.¹ The neutral ammonium salts of the three toluic acids can thus be prepared in ether, but not in methyl or ethyl alcohols on account of their great solubility in these solvents. They form white, crystalline precipitates, which are all soluble in water, acetone and acetic acid. They are less soluble in acetone than in the other solvents. They are stable in dry air and give off ammonia slowly in moist air. The *o*-toluate does not deliquesce, while the *m*- and *p*-salts do so very slightly. Their aqueous solutions are neutral.

The Chlorobenzoic Acids.

Ammonium *o*-Chlorobenzoate.—Rivals² mentions this salt as soluble in water with the absorption of a small amount of heat, but does not describe the method of preparation, the analysis nor the properties of it. Korczynski³ states that solid *o*-chlorobenzoic acid combines with ammonia under pressure, forming $C_6H_4ClCOONH_4$, and that a second molecule of ammonia is taken up at -15° , which is quickly given off as the temperature rises to normal.

This salt can be prepared by the method described, in an ether solution of the acid, as a fine, white powder. It is very soluble in water, methyl alcohol, ethyl alcohol, acetone and acetic acid. It is only slightly soluble in ether. A solution of the salt in water is neutral, and does not hydrolyze even on long standing. The salt is not hygroscopic, and gives off ammonia only very slowly in both dry and moist air.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Found: 8.01% N.

Ammonium *m*-Chlorobenzoate.—Gluud and Kempf⁴ have prepared this salt by heating the hydroxylamine salt of the acid to 170° , treating the mixture of the salt and the free acid obtained with warm xylene to remove the acid, extracting the ammonium salt with warm acetone, and then precipitating it with petroleum ether. It crystallized in small leaflets, which melted and decomposed at $203-204^\circ$ after a short sintering. It dissolved in cold water, and in some organic solvents on heating, but so readily evolved ammonia that little but the free acid itself remained in solution. An aqueous solution of the salt also gave off ammonia on heating, and the acid crystallized out on cooling. They also prepared the salt by passing ammonia into a solution of the acid in methyl alcohol, and precipitating it with ether. They thus obtained glistening scales. No analysis was made of the salts obtained. Their first method of preparation could not have given a very pure product, since it depended on the selective solubility of the free acid and the salt, and since the solutions

¹ McMaster, *THIS JOURNAL*, 36, 1924 (1914).

² *Ann. chim. phys.*, [7] 12, 521 (1897).

³ *Ans. Akad. Wissenschaften*, Krakau, 633 (1908); *Chem. Zentr.*, 2, 2009 (1908).

⁴ *J. Chem. Soc.*, 103, 1533 (1913).

of the salt gave off ammonia on warming, even slightly so at ordinary temperatures.

This salt can easily be prepared by passing dry ammonia into an ether solution of *m*-chlorobenzoic acid. There is formed a fine, white, amorphous precipitate, which, when crystallized from alcohol, gives a crystalline powder. It is readily soluble in water, methyl alcohol and ethyl alcohol, and slowly so in acetic acid. It is insoluble in ether. The aqueous solution is at first neutral, but very slowly becomes acid. The salt does not give off ammonia in dry air, but is slightly deliquescent.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Found: 8.01% N.

Ammonium *p*-Chlorobenzoate.—This salt was also prepared by Korczynski¹ by the same method used in the preparation of the *o*-compound. It can be prepared by passing ammonia into a saturated alcoholic solution of the acid. Glistening white laminae are thus formed. Upon passing ammonia into a solution of the acid in ether, a gelatinous precipitate is formed, which soon changes to a fine, amorphous powder. This can be crystallized from acetone in the form of very fine needles. The salt is soluble in water, methyl and ethyl alcohols, and acetic acid. It is also somewhat soluble in acetone. The solution of the salt in water is at first neutral, but hydrolyzes slowly on long standing. The salt does not deliquesce, and gives off ammonia only slowly in moist air.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Prepared in ether. Found: 7.98% N.
Prepared in ethyl alcohol. Found: 8.04% N.

The three chlorobenzoates can thus be readily prepared in ether. The *p*-salt can also be prepared in a saturated alcoholic solution of the acid. They are all soluble in water, methyl and ethyl alcohols and acetic acid. They are also soluble in acetone, but to a less extent than in the alcohols and acetic acid. The *p*-salt is the least soluble of the three. The aqueous solutions of the *m*- and *p*-salts become slowly acid, but that of the *o*-salt is very stable. Only the *m*-salt is slightly hygroscopic, and all three give off ammonia very slowly in the air.

The Bromobenzoic Acids.

Ammonium *o*-Bromobenzoate.—No reference to this salt can be found in the literature. It can be prepared by passing dry ammonia into an ether solution of *o*-bromobenzoic acid. The salt at first precipitates as a slightly gelatinous mass, which soon changes to an amorphous powder. If ammonia is passed into an alcoholic solution of the acid, or into a solution of the acid in a mixture of equal volumes of ether and ethyl alcohol no precipitate is formed; but if the latter solution is allowed to evaporate in the air, the salt forms in crystalline tablets. The salt can also be prepared by passing ammonia into a solution of the acid in benzene, from which it precipitates slowly. A flocculent precipitate forms at first and

¹ *Loc. cit.*

then changes to a fine powder. When recrystallized from benzene it forms in fan-like groups of needles.

The salt is soluble in water, methyl and ethyl alcohols and acetic acid. It is slightly soluble in acetone and insoluble in ether. The aqueous solution is neutral to sensitive litmus, there being no hydrolysis even on standing for several days. The salt is not deliquescent, is stable in dry air, and gives off ammonia very slowly in moist air. Analysis proved it to be the neutral anhydrous salt.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Prepared in ether. Found: 6.41% N.

Prepared in benzene. Found: 6.38% N.

Ammonium *m*-Bromobenzoate.—As in the case of the *o*-bromobenzoate, no reference to this salt can be found in the literature. It can be readily prepared in an alcohol-ether or in an ether solution of the acid. In the former it precipitates as silky, crystalline flakes, and in the latter as a lustrous white, semicrystalline powder. It is very soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is very slightly soluble in chloroform and appreciably so in acetone, but insoluble in ether. The salt is not at all deliquescent. It gives off ammonia very slowly in dry air, and slightly more rapidly in moist air. The salt can also be precipitated in benzene as a milky white, colloidal mass. Analysis was made of the salt prepared in ether.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Found: 6.38% N.

Ammonium *p*-Bromobenzoate.—This salt has been prepared by Korczynski¹ by the method described. It was prepared by us by passing ammonia into a solution of the acid in ether, in which it formed as a white, amorphous compound. No precipitate was formed when the ammonia was passed into an alcoholic solution of the acid, but on evaporation aggregates of beautiful crystalline plates were formed. The salt is slightly soluble in cold water, but readily soluble in hot water. It is also soluble in methyl alcohol, ethyl alcohol, and acetic acid. It is slightly soluble in acetone and in chloroform. The solution in water is neutral at first, but hydrolyzes slowly and becomes acid. The salt is not deliquescent, but gives off ammonia slowly in the air.

Analysis of the salt prepared in ether proved it to have the composition of the neutral salt.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Found: 6.46% N.

The neutral ammonium salts of the three bromobenzoic acids can thus be prepared in ether. The *o*-salt can also be prepared in benzene and the *m*-salt in an alcohol-ether mixture. They are soluble in water (the *p*-salt only appreciably so in hot water), methyl and ethyl alcohols, and acetic acid. They are slightly soluble in acetone and insoluble in ether. None of the salts are deliquescent.

¹ *Loc. cit.*

The Nitrobenzoic Acids.

Ammonium *o*-Nitrobenzoate.—Korczynski¹ has also prepared this salt. It can also be prepared by conducting dry ammonia into a solution of the acid in anhydrous ether, or into a saturated solution of the acid in ethyl alcohol. It forms as a slightly yellowish white, amorphous precipitate in ether or as a white, finely crystalline compound, having a decidedly yellowish tinge, in alcohol. It is soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is moderately soluble in acetone. The salt is only slightly hygroscopic, and imparts a neutral reaction to a water solution of it. The aqueous solution slowly hydrolyzes. The salt is fairly stable in the air, losing its ammonia but slowly in moist air.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Prepared in ether. Found: 7.69% ammonium N.
Prepared in ethyl alcohol. Found: 7.59% ammonium N.

Ammonium *m*-Nitrobenzoate.—Beilstein mentions the acid ammonium salt, $NH_4C_7H_4(NO_2)O_2 + C_7H_5(NO_2)O_2$. Korczynski¹ says that *m*-nitrobenzoic acid takes up one molecule of ammonia at room temperature and an additional molecule at 0° to -15°.

When ammonia is passed into a solution of *m*-nitrobenzoic acid in ether, the neutral ammonium salt forms as a finely crystalline, snow-white precipitate, soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is insoluble in ether. Its solution in water is neutral. The salt is stable in both dry and moist air. Both the ammonium nitrogen and the total nitrogen in this salt were determined.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.57% ammonium N.
Calc. for $C_7H_5N_2O_4$: 15.22%. Found: 15.20% total N.

Ammonium *p*-Nitrobenzoate.—Wilbrand and Beilstein² prepared this salt by dissolving the acid in concentrated ammonia water, and allowing the solution to evaporate to crystallization. A hot solution of the salt produced, upon cooling, faint rose-red, much streaked, very glittering, leaf-like crystals which were very easily decomposed. Korczynski¹ also mentions this salt, but does not give its properties. We obtained this salt by our method in an ether solution as a snow-white, amorphous powder, which on analysis proved to be the neutral salt. Some of the salt was recrystallized from warm water in the form of small, transparent leaflets. This was not analyzed, but it was probably the acid salt, as the aqueous solution of the normal salt, which is neutral at first, quickly hydrolyzes and becomes acid, especially on warming. The color mentioned by Wilbrand and Beilstein must have been due to impurities.

The neutral salt is soluble in water, slowly soluble in ethyl alcohol, readily soluble in methyl alcohol and moderately soluble in acetone. It is insoluble in ether. It is not deliquescent and does not lose ammonia in the air.

¹ *Loc. cit.*

² *Ann.*, 128, 261 (1863).

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.58% ammonium N.

The three nitrobenzoates can thus be prepared in ether. They are soluble in water, in the common alcohols, and in acetic acid. They are less soluble in acetone than in the other solvents mentioned. Of the three, the *p*-salt is the least soluble in the organic solvents.

Ammonium 3,5-Dinitrobenzoate.—Mention is made of this salt by Korczynski.¹ Hubner² states that he used this salt in solution to prepare silver and copper *m*-dinitrobenzoates. He did not prepare the solid ammonium salt.

It can be prepared by passing ammonia into an ether solution of the acid as a white, amorphous powder, having a slight yellowish tinge. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid, benzene and carbon tetrachloride. It is somewhat soluble in acetone, but less so than in the other solvents mentioned. It is insoluble in ether. The salt is not deliquescent. It is stable in dry air, but loses its ammonia very slowly in moist air. Its aqueous solution is neutral, and does not hydrolyze even on standing for several days.

Calc. for $C_7H_3N_2O_6(NH_4)$: 6.12%. Found: 6.11% ammonium N.

The Aminobenzoic Acids.

Ammonium *o*-Aminobenzoate.—This salt can be prepared either in ether or in a mixture of one volume of acetone and two volumes of ether. When prepared in ether, it is a white, amorphous powder, while in the acetone-ether mixture it forms fine, white needles. It is very soluble in water, the solution being neutral at first but soon becoming acid. The salt is also very soluble in methyl and ethyl alcohols and acetic acid. It is moderately soluble in acetone, and only slightly so in ether. It is slightly deliquescent. It does not lose ammonia in dry air, and only slowly in moist air.

Calc. for $C_7H_7N_2O_4$: 18.18%. Found: 18.14% total N.

This analysis was made on the salt prepared in ether and proved that we had obtained the neutral ammonium salt. Although some of the salts of *o*-aminobenzoic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

Ammonium *m*-Aminobenzoate.—As in the case of the ammonium *o*-aminobenzoate, no reference to this salt can be found in the literature. It can be prepared by pouring a saturated solution of the acid into absolute ethyl alcohol, into which dry ammonia has been passed for some time, into a large amount of ether. Although the salt is only slightly soluble in ether, it cannot be prepared directly in ether since the free acid is also only slightly soluble in that solvent. While filtering off the salt, prepared as above described, it is necessary to keep the alundum crucible

¹ *Loc. cit.*

² *Ann.*, 222, 78 (1883).

The Nitrobenzoic Acids.

Ammonium *o*-Nitrobenzoate.—Korczynski¹ has also prepared the salt. It can also be prepared by conducting dry ammonia into a solution of the acid in anhydrous ether, or into a saturated solution of the acid in alcohol. It forms as a slightly yellowish white, amorphous powder in ether or as a white, finely crystalline compound, having a slightly yellowish tinge, in alcohol. It is soluble in water, methyl alcohol, and acetic acid. It is moderately soluble in acetone. It is only slightly hygroscopic, and imparts a neutral reaction to a solution of it. The aqueous solution slowly hydrolyzes. The salt is stable in the air, losing its ammonia but slowly in moist air.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Prepared in ether. Found: 7.69% N.
Prepared in ethyl alcohol. Found: 7.59% ammonium N.

Ammonium *m*-Nitrobenzoate.—Beilstein mentions the ammonium salt, $NH_4C_7H_4(NO_2)O_2 + C_7H_5(NO_2)O_2$. Korczynski¹ states that nitrobenzoic acid takes up one molecule of ammonia at room temperature and an additional molecule at 0° to -15°.

When ammonia is passed into a solution of *m*-nitrobenzoic acid, the neutral ammonium salt forms as a finely crystalline precipitate, soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is insoluble in ether. Its solution in water is neutral. The salt is stable in both dry and moist air. Both the ammonium content and the total nitrogen in this salt were determined.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.57% ammonium N.
Calc. for $C_7H_5N_2O_4$: 15.22%. Found: 15.20% total N

Ammonium *p*-Nitrobenzoate.—Wilbrand and Beilstein prepared the salt by dissolving the acid in concentrated ammonia and then evaporating the solution to crystallization. A hot solution was produced, upon cooling, faint rose-red, much streaked, leaf-like crystals which were very easily decomposed. Beilstein mentions this salt, but does not give its properties. We prepared the salt by our method in an ether solution as a snow-white powder, which on analysis proved to be the neutral salt. The salt was recrystallized from warm water in the form of leaflets. This was not analyzed, but it was probably identical with the aqueous solution of the normal salt, which is neutral and slowly hydrolyzes and becomes acid, especially on warming. The method by Wilbrand and Beilstein must have been due to impurity.

The neutral salt is soluble in water, slowly soluble in methyl alcohol and moderately soluble in ether. It is not deliquescent and does not lose ammonia in the air.

¹ *Loc. cit.*

² *Ann.*, 128, 261 (1863).

and normal butane. A previous communication by the authors gave vapor pressures for ethane and ethylene. The method of experimentation was detailed in that communication. The same method was followed in this later work. The thermometers were calibrated at additional points in order to measure the higher temperatures demanded. These points are the melting points of chloroform, mercury and ice. Henning¹ found the following values for chloroform and mercury: Mercury, -38.89° ; chloroform, -63.7° .

The temperature readings as made by the authors with their pentane thermometers at the melting points of chloroform, mercury and ice are as follows:

Therm. No. 504: Chloroform -64.0 ; Mercury -36.5 ; Ice $+1.4$.

Therm. No. 707: Chloroform -67.1 ; Mercury -38.4 ; Ice $+1.3$.

These readings are uncorrected and are simply given to show how the thermometers varied among themselves.

In addition to using pentane thermometers, a calibrated mercury thermometer² was used in determining the normal boiling point and a few other points on the vapor-pressure curve of *N*-butane.

The chloroform used was Kahlbaum's purest reagent. Mercury was prepared by fractionating it by the method of Hulett.³ No differences in the melting points of these substances were found by additional fractionation of them.

Preparation of Gases.

Propane was prepared by the action of propyl iodide on a zinc-copper couple. It was purified by fractional distillation in a vacuum at the temperature of liquid air to rid it of air or other substances of high vapor pressure at that temperature, and at a temperature of -110° to remove water vapor and other substances whose vapor pressures are practically negligible at -110° . Phosphorus pentoxide was also used to remove water vapor. Propylene was prepared by dropping propyl alcohol on phosphorous pentoxide at ordinary temperature. *N*-Butane was prepared by the action of *N*-butyl iodide on a zinc-copper couple. Both of these gases were purified in essentially the same manner as the propane. Purification was carried to a point at which the entire liquid distilled at a temperature constant to $\pm 0.2^{\circ}$.

In the tables are shown the vapor pressures of the three substances, the equations of the curves, pressures calculated from the equations,

¹ Henning, F., "The Fixation of the Temperature Scale between 0° and -193° ," *Ann. Physik.*, [4] 43, 282-94 (1914).

² Calibrated by J. K. Clement, physicist of this Bureau.

³ *Phys. Rev.*, 34, 34 (1911).

VAPOR PRESSURE OF *N*-BUTANE AT LOW TEMPERATURES.
Temperature.

Pentane thermometer. 707 °C.	Pentane thermometer. 504 °C.	Mercury thermometer. °C.	Average.		Pressures.	
			°C.	° Abs.	Observed. Mm. Hg.	Calculated. Mm. Hg.
-0.3	-0.3	-0.2	-0.3	272.8	760	760
-1.6	-1.5	-1.4	-1.5	271.6	730	731
-2.9	-2.8	-2.7	-2.8	270.3	700	701
-4.9	-5.1	...	-5.0	268.1	650	652
-7.2	-7.1	...	-7.2	265.9	600	604
-12.2	-12.3	...	-12.3	260.8	500	504
-18.2	-18.0	...	-18.1	255.0	400	404
-25.3	-25.3	...	-25.3	247.8	300	300
-34.6	-34.7	...	-34.6	238.5	200	196
-40.4	-40.3	...	-40.3	232.8	150	148
-47.4	-47.6	...	-47.5	225.6	100	100
-58.3	-58.2	...	-58.3	214.8	50	52
-65.5	-65.3	...	-65.4	207.7	31	32
-76.1	-75.2	...	-75.6	197.5	15	15
-85.4	-85.1	...	-85.3	187.8	7	7
-93.3	-93.1	...	-93.2	179.9	3	3
-100.0	-99.8	...	-99.9	173.2	1	1
.....	-113.1	160.0	...	0.31

The results may also be expressed by plotting the logarithm of the pressure against the reciprocal of the absolute temperature, (Fig. 2). The

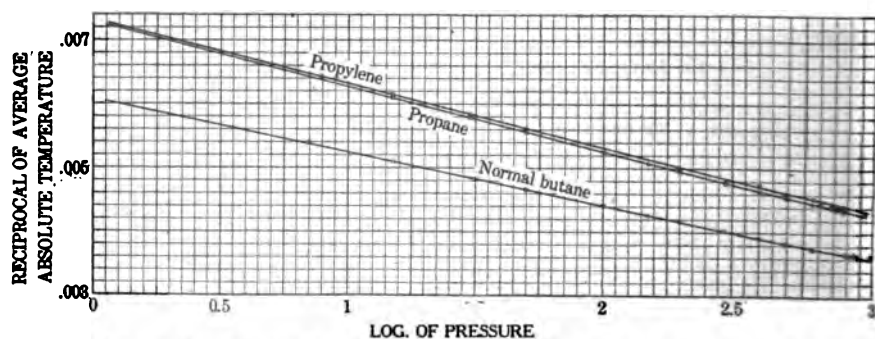


Fig. 2.—Curves showing the logarithm of the pressure plotted against the reciprocal of the absolute temperature.

straight lines shown were drawn by obtaining an equation from the average of all the results computed by the method of least squares and drawing the lines according to these equations.

For propylene the equation is: $\log P = -\frac{1006.1}{T} + 7.173.$

For propane: $\log P = -\frac{983.7}{T} + 7.3402.$

ESTIMATION OF RAFFINOSE BY ENZYMIC METHOD.

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Normal butane: $\log P = - \frac{1224.5}{T} - 7.364$.

Heat of Evaporation of Propane, Propylene and Isobutane
 Heat of evaporation over the temperature range 200°K to 300°K
 molecule, were calculated from the Clausius-Clapeyron equation:

$$\log \frac{P_2}{P_1} = \frac{H_v}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

By this equation and assuming the H_v to be constant, the
 H_v for propane, propylene and isobutane were calculated from
 the known P_1 and P_2 at T_1 and T_2 .

Normal temperature: $T = 273.15$ °K.
 $P_1 = 1000$ mm.
 $P_2 = 383.7$ mm.
 $T_2 = 243.15$ °K.

For propane: $H_v = 10,000$ cal/mole.
 For propylene: $H_v = 9,500$ cal/mole.
 For isobutane: $H_v = 9,000$ cal/mole.

For normal butane: $H_v = 10,500$ cal/mole.
 For isobutane: $H_v = 10,000$ cal/mole.

For normal butane: $H_v = 10,500$ cal/mole.
 For isobutane: $H_v = 10,000$ cal/mole.

For normal butane: $H_v = 10,500$ cal/mole.
 For isobutane: $H_v = 10,000$ cal/mole.

For normal butane: $H_v = 10,500$ cal/mole.
 For isobutane: $H_v = 10,000$ cal/mole.

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 nty-four hours. In
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 drolisis by emulsin. Up
 for the necessary experi-

The analysis of the salts consisted in determining the nitrogen by either the regular or a modified Kjeldahl method. In all the salts, except those of the three amino acids, the nitrogen present as "ammonium" nitrogen was determined. This is equal to the total nitrogen, except for the nitro acids. For the three amino acids, total nitrogen was determined. In the case of the *m*-nitro acid, both total and ammonium nitrogen were determined.

The Toluic Acids.

Ammonium *m*-Toluate.—No record can be found of the preparation and properties of this salt. It was prepared by passing dry ammonia gas into an ether solution of *m*-toluic acid. On passing in the gas, there was first formed an amorphous powder which, after a time, became crystalline. The powder, after being filtered, washed with ether and dried, was dissolved in ethyl alcohol, from which it recrystallized in the form of long prismatic needles. It crystallizes from acetone in the same form. It is readily soluble in water, to which it imparts a neutral reaction. It is easily soluble in methyl alcohol, ethyl alcohol and acetic acid. It is also soluble in acetone but a little less so than in the last named solvent. The salt is somewhat hygroscopic, and gives off ammonia in the air. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.19% N.

Ammonium *p*-Toluate.—Noad¹ prepared this salt by neutralizing an aqueous solution of the acid and allowing the solution to evaporate. The salt crystallized out in the form of small prisms. No analysis was made of the salt. Lossen² found that the neutral salt could be prepared, in the form of clear, flat cubes, by cautious evaporation of a solution of the acid in ammonia water. He also obtained it in glittering leafy crystals, upon the addition of an excess of alcoholic ammonia to an alcoholic solution of the acid. If an aqueous solution of this salt were boiled and the solution allowed to cool, needle-shaped crystals of the acid salt were obtained which crystallized from alcohol in the form of large silvery white glistening leaves.

We prepared this salt by passing dry ammonia into an ether solution of *p*-toluic acid. It precipitated as a fine, white, crystalline powder, which formed small needles when recrystallized from alcohol. The salt is soluble in water, methyl alcohol, ethyl alcohol, acetone and acetic acid. It is insoluble in ether. The aqueous solution of the salt is at first neutral but slowly becomes acid, due to hydrolysis. The salt is only slightly hygroscopic, and gives off ammonia slowly in moist air.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.06 and 9.11% N.

¹ *Ann.*, 63, 296 (1847).

² *Ibid.*, 298, 72 (1897).

stated, upon the measurement of step (2) in the enzymotic hydrolysis (see diagram). This is indeed a measurement of the cleavage of the same union which Neuberg, and also Bourquelot and Bridel, have selected, but there is an important difference between the methods because the melibiase which we employ, prepared from bottom yeast, is free from enzymes that hydrolyze glucosides. Tests have also shown that the melibiase solution does not contain maltase, cellase, lactase, trehalase, inulase or diastase. It does contain a very powerful invertase and so far it has not been possible to remove this enzyme. But removal is not necessary since top yeast yields an extract which is rich in invertase and quite free from melibiase, and this top yeast extract can be used to complete step (1), whereupon an accurate measurement of step (2), and the consequent estimation of raffinose from it, may be carried out. The only interfering substance of which we are aware is melibiose itself,¹ which would be estimated as raffinose by the method. Since melibiose reduces Fehling's solution and raffinose does not, it is possible to exclude it from consideration in some cases. Thus an aqueous extract from cottonseed, or its meal, contains almost no reducing sugar but much raffinose; and low-grade beet sugars are nearly free of reducing substances but often contain raffinose. The method appears sufficiently conclusive, therefore, for the estimation of raffinose in these products which are the best-known sources of the sugar. In the analysis of plant material and sugar mixtures in general, the method serves for the determination of raffinose and melibiose but does not distinguish them.

Directions for Performing the Analysis.—The solution in which raffinose is to be estimated is first clarified, if necessary, with neutral lead acetate and the excess of lead removed as oxalate or sulfide. It is advisable to dilute the solution, if necessary, so that the total sugars are not over 13%, because the enzymotic hydrolysis becomes very slow at higher sugar concentrations. The solution must be slightly acid to permit the action of the enzymes, but any free mineral acidity is to be avoided. It is recommended, in general, that solutions be accurately neutralized and subsequently acidified with one or two drops of glacial acetic acid per 100 cc. To 95 cc. of the sugar solution which has been prepared in the manner specified, 5 cc. of top yeast invertase solution, prepared as directed (see first reference), are added, a few cc. of toluene are shaken with the mixture to prevent the growth of microorganisms and it is kept at room temperature until its rotation becomes constant. The time which is required will depend primarily upon the activity of the enzyme solution, but as a rule constant rotation is reached over night or in twenty-four hours. In

¹ It may be found that stachyose contains a union which is hydrolyzed by melibiase, since Bourquelot and Bridel (*loc. cit.*) have observed its hydrolysis by emulsin. Up to the present we have not been able to secure any stachyose for the necessary experiments.

of the salt gave off ammonia on warming, even slightly so at ordinary temperatures.

This salt can easily be prepared by passing dry ammonia into an ether solution of *m*-chlorobenzoic acid. There is formed a fine, white, amorphous precipitate, which, when crystallized from alcohol, gives a crystalline powder. It is readily soluble in water, methyl alcohol and ethyl alcohol, and slowly so in acetic acid. It is insoluble in ether. The aqueous solution is at first neutral, but very slowly becomes acid. The salt does not give off ammonia in dry air, but is slightly deliquescent.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Found: 8.01% N.

Ammonium *p*-Chlorobenzoate.—This salt was also prepared by Korynski¹ by the same method used in the preparation of the *o*-compound. It can be prepared by passing ammonia into a saturated alcoholic solution of the acid. Glistening white laminae are thus formed. Upon passing ammonia into a solution of the acid in ether, a gelatinous precipitate is formed, which soon changes to a fine, amorphous powder. This can be crystallized from acetone in the form of very fine needles. The salt is soluble in water, methyl and ethyl alcohols, and acetic acid. It is also somewhat soluble in acetone. The solution of the salt in water is at first neutral, but hydrolyzes slowly on long standing. The salt does not deliquesce, and gives off ammonia only slowly in moist air.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Prepared in ether. Found: 7.98% N.
Prepared in ethyl alcohol. Found: 8.04% N.

The three chlorobenzoates can thus be readily prepared in ether. The *p*-salt can also be prepared in a saturated alcoholic solution of the acid. They are all soluble in water, methyl and ethyl alcohols and acetic acid. They are also soluble in acetone, but to a less extent than in the alcohols and acetic acid. The *p*-salt is the least soluble of the three. The aqueous solutions of the *m*- and *p*-salts become slowly acid, but that of the *o*-salt is very stable. Only the *m*-salt is slightly hygroscopic, and all three give off ammonia very slowly in the air.

The Bromobenzoic Acids.

Ammonium *o*-Bromobenzoate.—No reference to this salt can be found in the literature. It can be prepared by passing dry ammonia into an ether solution of *o*-bromobenzoic acid. The salt at first precipitates as a slightly gelatinous mass, which soon changes to an amorphous powder. If ammonia is passed into an alcoholic solution of the acid, or into a solution of the acid in a mixture of equal volumes of ether and ethyl alcohol no precipitate is formed; but if the latter solution is allowed to evaporate in the air, the salt forms in crystalline tablets. The salt can also be prepared by passing ammonia into a solution of the acid in benzene, from which it precipitates slowly. A flocculent precipitate forms at first and

¹ *Loc. cit.*

TABLE I.—ESTIMATION OF RAFFINOSE IN THE PRESENCE OF SUCROSE.
Sugars in 100 cc. solution (grams).

Number.	Sucrose added.	Raffinose.			Polarizations (corrected).		
		Added.	Found (H. & H.).	Found (Creydt).	Original.	After first hydrolysis.	After second hydrolysis.
1	12.98	0.032	0.042	0.047	+50.12	—16.09	—16.21
Duplicate	12.98	0.032	0.039	0.047	+50.12	—16.09	—16.20
2	12.94	0.065	0.049	0.070	+50.19	—15.97	—16.11
Duplicate	12.94	0.065	0.060	0.072	+50.16	—15.95	—16.12
3	12.88	0.130	0.127	0.148	+50.39	—15.57	—15.93
Duplicate	12.88	0.130	0.144	0.148	+50.40	—15.57	—15.98
4	12.75	0.260	0.239	0.268	+50.87	—15.01	—15.69
5	12.62	0.390	0.363	0.403	+51.25	—14.33	—15.36
6	12.35	0.649	0.648	0.675	+52.16	—13.00	—14.84
7	11.71	1.30	1.27	1.26	+53.25	—9.85	—13.46
8	11.05	1.95	1.89	1.97	+56.31	—6.64	—12.02
9	10.40	2.59	2.48	2.60	+58.45	—3.56	—10.61
10	9.10	3.89	3.72	3.89	+62.65	+2.81	—7.75

The top yeast extract read $+4.97^\circ$ in a 2 dcm. length, the bottom yeast extract $+2.56^\circ$. The tube length was 2 dcm. for all the readings, the temperature was accurately 20° , and the rotations refer to degrees Ventzke. Column 4 is calculated from the polarization differences between the last two columns, as has been described. By comparison of Columns 3 and 4, it will be seen that the estimation of raffinose is quite satisfactory, and that it appears possible to determine raffinose with fair accuracy even in case 100 parts of sucrose are mixed with only 0.5 part of raffinose.

The estimation of raffinose in the presence of sucrose may also be made according to the method of Creydt¹ from a knowledge of the polarizations before and after the first hydrolysis. The fifth column of the table records the amounts of raffinose which may be calculated from the Herzfeld formula of the Creydt method, $R = \frac{0.3266 P + P'}{1.554}$, in which R

is the percentage of raffinose, P the direct polarization of the normal weight (26 g. per 100 cc. solution), and P' the polarization after the first hydrolysis. The agreement with the known values may be somewhat better by the Creydt method than by the procedure which we propose, but it is to be remembered that the Creydt method is not applicable in case any optically active substances other than sucrose and raffinose are present. On the other hand, there is apparently no reason for supposing that the estimation of raffinose in the presence of any other sugars

¹ Z. Ver. d. Zuckerind., 37, 153 (1887). For a full discussion of this method, see C. A. Browne's "Handbook of Sugar Analysis," 1912 edition, p. 282. The authors express their thanks to Dr. Browne for calling their attention to the fact that Creydt's method, with Herzfeld's modification, is quite applicable to the data recorded in the table, although that method presupposes an inversion of the sucrose and raffinose by acid hydrolysis, and the data result from enzymotic hydrolysis.

The Nitrobenzoic Acids.

Ammonium *o*-Nitrobenzoate.—Korczynski¹ has also prepared this salt. It can also be prepared by conducting dry ammonia into a solution of the acid in anhydrous ether, or into a saturated solution of the acid in ethyl alcohol. It forms as a slightly yellowish white, amorphous precipitate in ether or as a white, finely crystalline compound, having a decidedly yellowish tinge, in alcohol. It is soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is moderately soluble in acetone. The salt is only slightly hygroscopic, and imparts a neutral reaction to a watery solution of it. The aqueous solution slowly hydrolyzes. The salt is fairly stable in the air, losing its ammonia but slowly in moist air.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Prepared in ether. Found: 7.69% ammonium N.
Prepared in ethyl alcohol. Found: 7.59% ammonium N.

Ammonium *m*-Nitrobenzoate.—Beilstein mentions the acid ammonium salt, $NH_4C_7H_4(NO_2)O_2 + C_7H_5(NO_2)O_2$. Korczynski¹ says that *m*-nitrobenzoic acid takes up one molecule of ammonia at room temperature and an additional molecule at 0° to -15°.

When ammonia is passed into a solution of *m*-nitrobenzoic acid in ether the neutral ammonium salt forms as a finely crystalline, snow-white precipitate, soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is insoluble in ether. Its solution in water is neutral. The salt is stable in both dry and moist air. Both the ammonium nitrogen and the total nitrogen in this salt were determined.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.57% ammonium N.
Calc. for $C_7H_5N_2O_4$: 15.22%. Found: 15.20% total N.

Ammonium *p*-Nitrobenzoate.—Wilbrand and Beilstein² prepared the salt by dissolving the acid in concentrated ammonia water, and allowing the solution to evaporate to crystallization. A hot solution of the salt produced, upon cooling, faint rose-red, much streaked, very glittering leaf-like crystals which were very easily decomposed. Korczynski¹ also mentions this salt, but does not give its properties. We obtained the salt by our method in an ether solution as a snow-white, amorphous powder, which on analysis proved to be the neutral salt. Some of the salt was recrystallized from warm water in the form of small, transparent leaflets. This was not analyzed, but it was probably the acid salt, as the aqueous solution of the normal salt, which is neutral at first, quickly hydrolyzes and becomes acid, especially on warming. The color mentioned by Wilbrand and Beilstein must have been due to impurities.

The neutral salt is soluble in water, slowly soluble in ethyl alcohol, readily soluble in methyl alcohol and moderately soluble in acetone. It is insoluble in ether. It is not deliquescent and does not lose ammonia in the air.

¹ *Loc. cit.*

² *Ann.*, 128, 261 (1863).

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.58% ammonium N.

The three nitrobenzoates can thus be prepared in ether. They are soluble in water, in the common alcohols, and in acetic acid. They are less soluble in acetone than in the other solvents mentioned. Of the three, the *p*-salt is the least soluble in the organic solvents.

Ammonium 3,5-Dinitrobenzoate.—Mention is made of this salt by Korczynski.¹ Hubner² states that he used this salt in solution to prepare silver and copper *m*-dinitrobenzoates. He did not prepare the solid ammonium salt.

It can be prepared by passing ammonia into an ether solution of the acid as a white, amorphous powder, having a slight yellowish tinge. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid, benzene and carbon tetrachloride. It is somewhat soluble in acetone, but less so than in the other solvents mentioned. It is insoluble in ether. The salt is not deliquescent. It is stable in dry air, but loses its ammonia very slowly in moist air. Its aqueous solution is neutral, and does not hydrolyze even on standing for several days.

Calc. for $C_7H_2N_2O_6(NH_4)$: 6.12%. Found: 6.11% ammonium N.

The Aminobenzoic Acids.

Ammonium *o*-Aminobenzoate.—This salt can be prepared either in ether or in a mixture of one volume of acetone and two volumes of ether. When prepared in ether, it is a white, amorphous powder, while in the acetone-ether mixture it forms fine, white needles. It is very soluble in water, the solution being neutral at first but soon becoming acid. The salt is also very soluble in methyl and ethyl alcohols and acetic acid. It is moderately soluble in acetone, and only slightly so in ether. It is slightly deliquescent. It does not lose ammonia in dry air, and only slowly in moist air.

Calc. for $C_7H_7N_2O_2$: 18.18%. Found: 18.14% total N.

This analysis was made on the salt prepared in ether and proved that we had obtained the neutral ammonium salt. Although some of the salts of *o*-aminobenzoic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

Ammonium *m*-Aminobenzoate.—As in the case of the ammonium *o*-aminobenzoate, no reference to this salt can be found in the literature. It can be prepared by pouring a saturated solution of the acid into absolute ethyl alcohol, into which dry ammonia has been passed for some time, into a large amount of ether. Although the salt is only slightly soluble in ether, it cannot be prepared directly in ether since the free acid is also only slightly soluble in that solvent. While filtering off the salt, prepared as above described, it is necessary to keep the alundum crucible

¹ *Loc. cit.*

² *Ann.*, 222, 78 (1883).

traction could in any case be observed with the 100 cc. samples of gas employed.

Carbon monoxide was also tested for, but none could be detected in 100 cc. samples by either ammoniacal cuprous chloride or hydrochloric acid cuprous chloride.

Oxygen was determined by absorption in the phosphorus pipet, but several checks were also made with alkaline pyrogallol.

For methane the Dennis combustion pipet was employed¹ which gave simultaneously a determination of the hydrogen present, but the hydrogen values were checked by the copper oxide method of Dennis.²

The residue of unabsorbable gas remaining upon completion of the analysis was called nitrogen. In the analyses tabulated below nitrogen has been taken by difference.

The Composition of the Gas.—As the concentration of peptone, meat or liver in lactose media increases, the volume of gas increases. This increase in gas volume is quite rapid up to 4% peptone, but after 5% peptone is reached, the increase is but slight in the volume percentage of gas collecting in the closed arm of the fermentation tubes. Preliminary experiments having shown that the composition of these gases remained substantially the same in the case of media having peptone concentrations above 5%, it was thought to be unnecessary to make complete gas analyses of the gases from all tubes of high peptone concentration, since CO₂ determinations alone would yield the information desired.

The averages of the results obtained are given in Table I.

TABLE I.

	Percentage of peptone in media.									
	1%.	2%.	3%.	4%.	5%.	6%.	7%.	8%.	9%.	10%.
Carbon dioxide.....	26.9	34.2	37.7	38.0	39.0	39.5	..	39.8	39	40
Hydrogen.....	70.2	63.2	62.3	58.3	59.0	60.5	..	60.2	61.0	60
Nitrogen.....	2.9	2.6	..	2.7	2.0
Methane.....	0	0	0	0	0	0	0	0	0	0
Heavy hydrocarbons.....	0	0	0	0	0	0	0	0	0	0
Carbon monoxide.....	0	0	0	0	0	0	0	0	0	0
Oxygen.....	0	0 ³	0	0 ³	0

In order to render easier the interpretation of these results the curves for the values of CO₂ and H have been plotted in Fig. 2.

The variations in the percentage composition of the gases obtained in different runs with media prepared at different times and inoculated with different sewage samples were less than we anticipated. In Table II are given the results obtained with gases from 4% peptone. These

¹ Dennis, "Gas Analysis," 1913 ed., 147.

² Dennis, *Ibid.*, 198.

³ In a single sample of both 2% and 4%, oxygen was present in from 0.1 to 0.2%.

analyses are typical examples of the variations obtained with other concentrations.

TABLE II.

	Lactose media.					Dextrose media.	
	1.	2.	3.	4.	5.	6.	7.
Carbon dioxide.....	38.0	38.1	38.6	35.0	37.2	38.8	38.4
Hydrogen.....	59.9	60.0	59.4	61.6	55.6	59.2	59.5
Nitrogen.....	2.0	1.9	2.0	3.4	6.6	2.0	2.1
Oxygen.....	0.1	0	0	0	0.6	0	0
Methane.....	0	0	0	0	0	0	0
Heavy hydrocarbons.....	0	0	0	0	0	0	0

Gas samples 1, 2, 3, 4 were obtained from the large tubes shown in Fig. 1. Sample 5 consisted of the gases collected from a large number of ordinary fermentation tubes, while Samples 6 and 7 are gas samples from

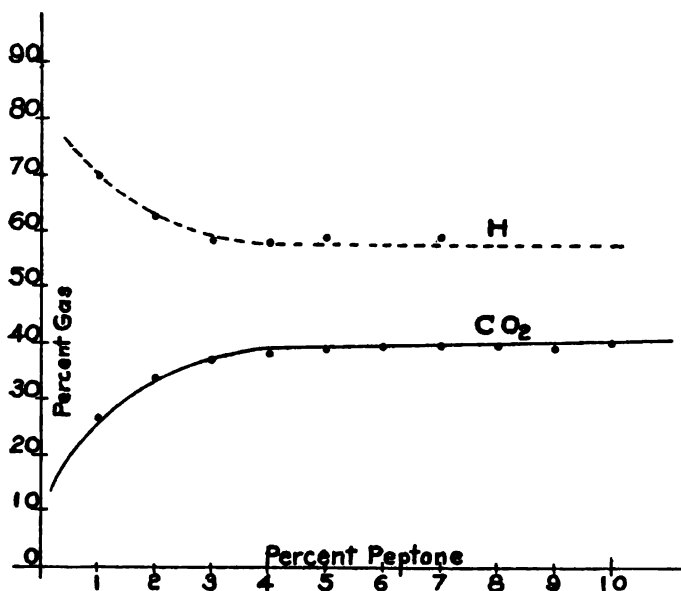


Fig. 2.

large tubes containing dextrose-peptone media, and have been incorporated in the table to afford a comparison between lactose and dextrose-containing media. It will be noted that the gases are substantially identical in character.

In only three cases was any evidence obtained of the presence of oxygen in the gases. Nor could we obtain any measurable volumes of CO₂ after combustion, showing, that if methane is present, it can be only in minute traces. It must be borne in mind, however, that these analyses were made as soon as the fermentation tubes reached the maximum fermentation,

i. e., as soon as the gases ceased to increase in volume, a condition usually reached at the end of from 20 to 26 hours.

This system of procedure was adopted so as to obtain as nearly as possible a correct gas composition. For it is obvious that upon standing for some hours there will be marked changes in the composition of the gases because of the relatively high solubility of CO_2 in aqueous solutions.

In the case of dextrose, Baginsky¹ was the first to point out that methane is sometimes formed, a fact later confirmed by Jesse.² It remained for Pennington and Küsel³ to prove that methane is formed only when oxygen is present in solution in the media: this they did by excluding oxygen from the bulb of the fermentation tube by attaching thereto an absorption tube containing alkaline pyrogallol.

Since the passage from the closed arm to the bulb or reservoir of our fermentation tubes was relatively small, we may properly consider that we have an anaerobic growth in the closed arm, and that therefore the observations of Pennington upon the fermentative action of the *B. coli* group upon dextrose is confirmed for lactose.

It occurred to us, in this connection, that it might be of interest to try and obtain a production of methane by introducing oxygen into media and tubes. With this end in view a number of experiments were tried, using media containing in one series 3.5% and in a second series 4% peptone, and in all cases 1% lactose, 0.6% potassium chloride and an acidity of 1%. Into the large fermentation tubes (Fig. 1) various volumes of pure sterile oxygen were introduced and, after inoculation with sewage, incubated at 38° for twenty-four to twenty-six hours. The gases obtained were then carefully analyzed. The results given in Table III may be considered as typical of the phenomena observed.

TABLE III.

	Media shaken with pure oxygen until saturated.	15 cc. pure oxygen in closed arm.		42 cc. pure oxygen in closed arm.		50 cc. pure oxygen in closed arm.	
		Composition.	Corrected for excess oxygen.	Composition.	Corrected for excess oxygen.	Composition.	Corrected for excess oxygen.
Gas formed.....	60.4	58.3	..	58.3	..	60.4	..
Carbon dioxide.....	39.6	40.4	42.3	31.9	42.4	30.7	41.3
Hydrogen.....	59.2	53.6	55.9	40.8	54.2	40.2	54.1
Methane.....	0.2	0.2	..	0.4	..	0.2	..
Heavy hydrocarbons.	0.0	0.0	..	0.0	..	0.0	..
Carbon monoxide....	0.0	0.0	..	0.0	..	0.0	..
Oxygen.....	0.1	4.25	..	24.8	..	25.7	..
Nitrogen.....	1.6	1.6	..	2.1	..	3.2	..

¹ Baginsky, *Z. physiol. Chem.*, 13, 352 (1889).

² Jesse, *Univ. Ill. Bull.*, 20, IX, 47 (1912).

³ Pennington and Küsel, *This Journal*, 22, 556 (1900).

These results appear to still further substantiate the results of Pennington and Küsel that it is only when oxygen is present that methane is formed, although we were able to obtain merely a very small yield of this gas with an atmosphere of pure oxygen and analyses made at the end of twenty-four hours.

It will be noted upon consulting Table II that the total volume of gas formed upon completion of fermentation, *including* the oxygen atmosphere in the tubes, was substantially constant, that is to say that when part of the closed arm of the fermentation tube is occupied by gas, less fermentation gases can collect therein. The gas volume is, therefore, as might be expected proportional to the volume of liquid in the closed arm, since it is only from this material that the gas can be formed and collect above the liquid. To prove this a large number of experiments were tried with fermentation tubes with enlargements of different capacities in the closed arms. In every instance the volumes of gas formed by sewage organisms were proportional to the volumes of culture media in the closed arms, and independent of the length of the closed arm.

A biochemic problem of great interest relative to mixed sewage floras is indicated by the results tabulated above. This is the relatively enormous quantity of oxygen utilized by these bacteria without very materially affecting the composition of the gases of fermentation, yet an excess of oxygen appears to be followed by an increased percentage of CO_2 and a decreased percentage of H. Although these biochemic questions had little bearing upon the main objects of the investigation it was thought that determinations of final acidity might indicate how the oxygen had been used by the microorganisms. Much to our surprise, no change in final acidity could be noted.

The "gas ratio" of an organism, as has been stated, is commonly expressed as the ratio of gas absorbed by potassium hydroxide to that unabsorbed by this reagent. The unabsorbed residue is generally called hydrogen, and the ratio expressed as $\text{CO}_2 : \text{H} = a : b$. The analyses given above indicate that the unabsorbed gas consists of hydrogen plus a small percentage of nitrogen and in rare cases some oxygen and perhaps methane. Calculated in the usual manner the average gas ratios which were obtained with lactose-peptone media determined as soon as fermentation ceased (20 to 26 hours), may be expressed as follows:

Peptone.....	1%	2%	3%	4%	5%	6%	8%	9%	10%
	1:2.71	1:1.92	1:1.65	1:1.63	1:1.56	1:1.53	1:1.51	1:1.56	1:1.50

We may, therefore, conclude that the "gas ratio" of a mixed sewage flora or of fecal bacteria will probably vary from $\text{CO}_2 : \text{H} = 1 : 3$ with low peptone concentrations to $\text{CO}_2 : \text{H} = 1 : 1.5$ (or perhaps even lower) with high peptone concentrations.

Standard lactose media made with 500 g. of meat per liter and 1%

peptone, comports itself toward this class of bacteria in a manner similar to media containing from 1.5 to 2% peptone. If, therefore, such media are inoculated with relatively large volumes of a water sample the concentration of nitrogenous material will be thereby reduced to a point such that fairly wide variations in the volumes of CO_2 , H, and gas ratios may be expected.

When high peptone concentrations to which meat had also been added were employed the gases obtained were usually about 2% higher in CO_2 than when meat was absent. A correspondingly lower percentage of hydrogen was then observed.

The presence of "enriching agents," such as bile, bile-salt, or phenol appeared to affect neither the total volume of gas formed nor the composition of these gases.

Pure cultures of *B. coli* isolated from sewage, from contaminated water and from the feces of horses, cows, calves, sheep and pigs gave gas volume and CO_2 percentages increasing with increasing peptone concentration similar to the values obtained with the mixed flora of sewage.

Summary.

1. The gases formed by fecal bacteria in lactose-peptone media increase in volume with an increase in peptone concentrations.
2. The percentage of CO_2 present in these gases of fermentation increases with an increase in peptone, meat or liver until an equivalent of approximately 4% peptone is reached, after which the CO_2 per cent. remains substantially constant.
3. Hydrogen decreases with a rise in peptone until 4 to 5% of peptone is reached after which the per cent. of this gas remains substantially constant.
4. The "gas ratio" varies with the concentration of the nitrogenous material present in the medium.
5. No methane appears to be formed unless oxygen (air) has free access to the media and the inoculated medium stands for over twenty-four hours.
6. A small but nearly constant amount of nitrogen is found in the gases of fermentation.
7. An excess of oxygen retards gas formation and tends to increase the percentage of CO_2 .
8. The total volume of gas formed is proportional to the volume of liquid contained in the closed arm of the fermentation tube.
9. The presence of enriching agents retards gas formation but does not materially alter the composition or total volume of gas formed.

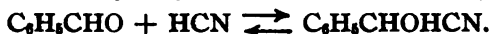
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF MCGILL UNIVERSITY.]

ENZYMES: THE SYNTHETIC AND HYDROLYTIC OXYNITRILASE. PART II.

By VERNON K. KRIEBLE.

Received July 8, 1915.

Rosenthaler¹ has recently published a series of papers which seemed to indicate that emulsin contains a synthetic as well as a hydrolytic enzyme for benzaldehyde-cyanhydrin. The contention that the hydrolytic enzyme is distinct from the synthetic is such a fundamental one in enzyme chemistry that it seemed worth while to investigate it still further, using quantitative methods. Bayliss,² has repeated certain of Rosenthaler's experiments and came to the conclusion that Rosenthaler's contention is not well founded. Bayliss' experiments, however, are not strictly parallel to those of Rosenthaler's and his conclusion is, therefore, hardly justified. Rosenthaler used emulsin which he subjected to various treatments and then studied its synthetic action on hydrocyanic acid and benzaldehyde, and its hydrolytic action on benzaldehydecyanhydrin.



Bayliss used glucose and glycerol to study the synthetic action and the corresponding glycerol glucoside to study the hydrolytic action. These reactions are quite distinct from each other. Rosenthaler's is one of addition while Bayliss' is a condensation reaction between an alcohol and glucose with the loss of water. This point seems important as it has not yet been proved that the oxynitrilase in emulsin is also the enzyme which splits glucose from the benzaldehydecyanhydrin in the glucoside amygdalin. In fact it seems very unlikely that oxynitrilase has this power, as the preparation of the enzymes from the leaf of *Prunus Serotina* does not hydrolyze salicin to glucose and the alcohol saligenin,³ or amygdalin into glucose or a disaccharide and the alcohol benzaldehydecyanhydrin. Whether it splits glucose from Fisher's mandelonitrile glucoside has not yet been determined. As Rosenthaler⁴ did not intend that his methods of treatment would distinguish the hydrolytic from the synthetic enzyme in any other case except the oxynitrilases, it is necessary to restrict oneself to the chemical reaction which he used, namely, the synthesis and hydrolysis of benzaldehydecyanhydrin. Unfortunately, the cyanhydrin reaction is a very tedious one to study. We spent considerable time in trying to develop methods of analysis in order that we might follow the rate of combination. The first method we used was to stop the reaction,

¹ *Biochem. Z.*, 28, 408 (1910); 50, 486 (1913); *Arch. Pharm.*, 251, 56 and 85 (1913).

² *J. Physiol.*, 46, 236 (1913).

³ Kriebel, *THIS JOURNAL*, 35, 1643 (1913).

⁴ *Biochem. Z.*, 59, 498.

extract the nitrile present, and then hydrolyze it with hydrochloric acid to mandelic acid. The mandelic acid was extracted with ether and the ether was boiled off and the mandelic acid dried to constant weight. As the mandelic acid was contaminated with benzoic acid it was necessary to dissolve it in water and make it up to a definite volume and then titrate an aliquot part in order to calculate the amount of pure mandelic acid. The method did not prove satisfactory, as mandelic acid forms an internal anhydride when evaporated in presence of traces of hydrochloric acid. The second method was more satisfactory and depended on the fact that when a nitrile is hydrolyzed with hydrochloric acid all the nitrogen is changed to ammonium chloride. The nitrile was extracted with ether and then hydrolyzed with hydrochloric acid as before. The hydrochloric acid solution was then made up to a definite volume and an aliquot portion transferred to a Kjeldahl distillation flask. It was made strongly alkaline and distilled into standard acid. From the amount of standard acid used one could calculate the amount of nitrile in the original solution. Before we tried this method very extensively, we came across a method devised by Wirth¹ which proved so very satisfactory that we used it exclusively in our later experiments. The method depends on the fact that dilute acid arrests the synthesis or hydrolysis of mandelonitrile completely. The amount of free hydrocyanic acid can then be estimated with the aid of silver nitrate and ammonium thiocyanate.

Another difficulty in studying this reaction is its sensitiveness to minute traces of acid. In our earlier experiments we prepared the benzaldehyde for each experiment by shaking up a suitable amount of the laboratory stock with bicarbonate of soda solution, then extracting it with ether, drying it over anhydrous sodium sulfate and then distilling, collecting the ether separately. We did not always, however, use the benzaldehyde once. Sometimes it was prepared several hours before we actually used it. In such cases the aldehyde would be kept in a small stoppered Erlenmeyer flask. We found that we could not get concordant results in this way and we finally traced the difficulty to the fact that the acidity of the aldehyde varied sufficiently to change the rate. We found, for example, that freshly distilled benzaldehyde required about 2 cc. of *N*/8 sodium hydroxide solution for neutralization, but if it was allowed to stand overnight in a stoppered bottle it frequently required 8 to 10 cc. of *N*/8 sodium hydroxide solution. We finally prepared a large amount of pure benzaldehyde by treating it with aqueous bicarbonate of soda as already described and then distilling it under reduced pressure directly into a buret. When we were finished with the distillation we flooded the apparatus with nitrogen, exhausted it, and then filled a second time. The buret was disconnected from the distillation apparatus and connected to a large

¹ *Arch. Pharm.*, 249, 382-400 (1911).

reservoir of nitrogen. The tip of the buret was continually kept immersed in water. When benzaldehyde was required the tip was washed and dried and, after running out 5 or 6 drops, the amount required for the experiment was withdrawn. In this way we had benzaldehyde for our experiments which did not vary more in acidity than 0.1 cc. of *N*/8 sodium hydroxide for 1 cc. of benzaldehyde.

The hydrocyanic acid was prepared by treating potassium ferrocyanide with sulfuric acid in a distilling flask and then boiling off the hydrocyanic acid and collecting it in distilled water. The aqueous acid was again placed in a distilling flask and the acid boiled off into distilled water. This operation of boiling off the hydrocyanic acid into distilled water was frequently repeated to keep it as pure as possible from decomposition products. The aqueous solution was always clear and colorless.

We spent much time in trying to prepare pure mandelonitrile but we frankly admit that we did not succeed, nor were we able to buy a pure specimen. We hope in a separate communication at a later date to give our results on the preparation of the nitrile. The nitrile which we used was made in the following way: 28 g. benzaldehyde, 87 cc. of 9.2% HCN and 120 cc. water were put into a glass stoppered bottle. Before closing, the bottle was flooded with nitrogen. It was shaken in a shaking machine for nearly 6 days when the theoretical amount of hydrocyanic acid for pure nitrile had disappeared. The oily layer was separated in a separating funnel. It was clear and colorless, but it was not pure nitrile, because when it was hydrolyzed it yielded only about 82% of the theoretical amount of ammonium chloride. When 1 cc. was added to 168 cc. of water it yielded only 13.7% of free HCN while if it had been pure it should have yielded 19% of free HCN on reaching the equilibrium point.

In our experiments we studied the rate of reaction and the equilibrium point between hydrocyanic acid and benzaldehyde in the presence of oxynitrilase to determine whether there was any difference in the enzyme obtained from various sources and also in the enzyme obtained from the same source, but by various methods and subjected to certain treatments. It is obvious that if there is a synthetic and a hydrolytic enzyme for a certain reaction there must be a difference in the equilibrium point. This point has been particularly emphasized by Bayliss.

Experimental.

The first point we investigated was to examine oxynitrilase from various sources. We extracted wild-cherry leaves (*Prunus Serotina*), and peach leaves collected in 1914. We also tried emulsins, one sample we extracted from the kernels in peach stones, another from sweet almonds, and the third was a preparation bought from Kahlbaum.

The experiments were carried out in a 225 cc. wide-mouthed bottle. It was closed with a cork which had three holes in it. Through one the

stirring rod passed, in the second we inserted a glass tube to pass nitrogen gas, and the third was used to pipet out definite amounts at various intervals of time. It was closed when not in use with another cork. The experiments were conducted in the following manner: 124 cc. of water was put into the bottle with 50 cc. of the enzyme solution and 1 cc. (1.02 g.) of benzaldehyde. The bottle was put into a bath kept at 25° and the contents of the bottle stirred. Before the stirring was started, however, nitrogen was passed through the flask for several minutes to insure that all the air was expelled. After a half hour, 25 cc. of HCN solution was added (containing 0.262 g. HCN) and the rate followed by pipeting out 20 or 25 cc. into a 100 cc. flask containing 5 cc. of $N/5$ $AgNO_3$ and 5 cc. of 4 N nitric acid. The flask was filled to the mark, the solution filtered, throwing away the first portion of the filtrate, and then titrating 50 cc. of the filtrate with a $N/30$ ammonium thiocyanate solution. Nitrogen was circulated through the bottle for thirty minutes after the hydrocyanic acid was added when the equilibrium was very nearly reached. Stirring was discontinued at this point, too, as the solution had become perfectly homogeneous.

The method is not altogether satisfactory. In the first place, the amount of benzaldehyde used does not completely dissolve in the amount of water used, so that the solution is not homogeneous at the beginning of the experiment. Consequently there is always the possibility of withdrawing equimolecular quantities of aldehyde and acid with the pipet. There is also the possibility that a certain amount of the aldehyde becomes oxidized during the first half hour before the hydrocyanic acid is added.

TABLE I.

	Millimoles of free HCN per liter.	
<i>Prunus Serotina</i> leaves extract from 2 g. .	9.1	
<i>Prunus Serotina</i> leaves acetone ppt. from extract of 2.5 g.	9.7	
Peach leaves acetone ppt. from 2 g.	9.2	Total millimoles of HCN
1 g. emulsin (Kahlbaum).....	10.0	added per liter at
1 g. emulsin from sweet almonds.....	9.0	Temperature 25° C.
1 g. emulsin from peach kernels.....	10.0	

The emulsin experiments were not so satisfactory, as 25 cc. of the solution gave such a bulky precipitate in the 100 cc. measuring flask that one could hardly tell when the liquid was exactly at the mark.

From these results one sees that the equilibrium point does not vary more than the experimental error and certainly shows no evidence of the presence of a synthetic or hydrolytic oxynitrilase. It is conceivable, however, that if there are two enzymes they always occur in the same ratio to each other. We, therefore, tried various lengths of time of

traction and also various amounts of water in the extraction to see if a solution could be obtained which gave a different equilibrium point. All the following experiments were carried out in the wide-mouthed bottle already described, at 25°.

Experiment 1.—2.5 g. wild-cherry leaves were extracted for 3 hours with 60 cc. of distilled water. The mixture was filtered and 50 cc. of the extract added to 124 cc. of distilled water and 25 cc. of hydrocyanic acid (0.262 g. HCN). When the temperature inside the bottle had reached 25°, 1 cc. (1.0285 g.) benzaldehyde was added. At the time indicated, 10 or 20 cc. were withdrawn and analyzed. The second line represents millimols of free hydrocyanic acid per L.

Minutes.....	13	52	134	313	1140	1800
	41.2	23.9	14.4	10.7	9.4	9.3

Experiment 2.—In this experiment the same amount of a similarly prepared enzyme solution was used but the method of the experiment was slightly changed. The enzyme solution and distilled water were put into the bottle, then it was flooded with nitrogen and 1 cc. benzaldehyde added. After 1½ hour of stirring the 25 cc. hydrocyanic acid were added.

Minutes.....	11	30	102	279	1020
	35.4	26.1	15.9	9.9	9.1

Experiment 3.—In this case, the 2.5 g. of leaves were extracted for 14 hours. Method same as in Experiment 1.

Minutes.....	11	29	85	234	464	1260	3300
	42.5	33.5	20.8	13.0	9.3	9.3	9.1

Experiment 4.—2.5 g. were extracted for 24 hrs. Method same as Experiment 1.

Minutes.....	9	36	145	320	1080
	40.6	33.7	16.8	11.8	9.7

Experiment 5.—In this experiment, 2.5 g. of wild-cherry leaves were extracted with 120 cc. of water for 3 hours and 100 cc. of the extract used instead of 50. Only 74 cc. of distilled water were used instead of 124. The method was same as Experiment 2.

Minutes.....	12	30	90	300	1080
	34.7	26.8	14.8	9.9	9.1

Experiment 6.—In this case, 5 g. of leaves were extracted with 60 cc. and 50 cc. used. Method as in Experiment 2.

Minutes.....	12	30	90	300	1080
	35.9	23.5	13.2	11.1	9.1

We carried out about 20 experiments with the extract of the same stock of ground leaves in which the nitrile was extracted and hydrolyzed and in every case the mandelic acid was found active, the percentage of active acid varying from 40 to 50% of the total mandelic acid produced.

Where the extract was boiled, the mandelic acid was inactive. This proves that the leaf actually contained active oxynitrilase.

In the third series of experiments we repeated some of the methods which Rosenthaler gave for separating the hydrolytic enzyme from the synthetic enzyme. We did not use emulsin as a source of our oxynitrilase because it does not produce a very active nitrile¹ and contains only a small amount of oxynitrilase. The rate for 1 g. of emulsin is approximately the same as for 75 mg. precipitated from the extract of 2 g. of peach leaves with acetone. We, therefore, used the extract from peach leaves. The benzaldehyde contained from 0.15% to 0.2% benzoic acid when titrated in 10 cc. alcohol with *N*/8 alkali, using phenolphthalein as an indicator. The following table gives the results tabulated in millimoles per liter:

TABLE II.

	5 min.	10 min.	15 min.	30 min.	24 hrs.	48 hrs.
1. Blank	45.7	44.9	43.8	40.5	..	9.6
2. Precipitated enzyme	26.1	17.6	16.4	14.3	9.2	No change
3. Precipitated enzyme	25.5	19.4	16.7	14.3	11.6	9.0
4. Precipitated enzyme boiled	39.7	36.5	32.2	27.6	14.6	...
5. Enzyme treated with HCN	25.5	18.6	16.1	13.9	9.8	9.1
6. Enzyme treated with benzaldehyde	20.4	16.5	14.2	12.9	9.8	9.3

The method was the same as described in Expt. 2 of the last series. *i. e.*, the enzyme solution and water were put into the bottle, the bottle placed in the water bath and flooded with nitrogen. 1 cc. of aldehyde was then added and the contents stirred for 1/2 hour before the 25 cc. of hydrocyanic acid were added.

Experiment 1 gives the rate at which benzaldehyde and hydrocyanic acid combine by themselves at this concentration.

The enzyme in Experiment 2 was prepared by adding 5 g. of ground peach leaves in a bottle and 120 cc. of water. The bottle was closed and placed in a shaking machine for 3 hours. The leaves were filtered through cotton wool placed on a Buchner funnel. To 100 cc. of the filtrate 250 cc. of acetone were added, shaking the beaker containing the extract during the addition. After a few minutes a light precipitate formed. This was filtered on a quantitative filter paper placed in a 4-inch Buchner funnel. Only slight suction was used in order not to draw the precipitate through the filter. The enzyme on the paper was washed first with about 20 cc. of 95% alcohol and then with an equal amount of ether. When we were ready to use it, we placed the filter paper in the bottom of a large beaker and added 75 cc. of water. The beaker was swirled occasionally for several hours. The solution was rinsed out with enough water to make the volume up to 100 cc. 50 cc. was used for each experiment and contained about 80 mg. of enzyme. The second 50 cc. was boiled for five

¹ Kriebel, *THIS JOURNAL*, 35, 1643 (1913).

minutes and then made up to 50 cc. again and used in Expt. 4. This experiment shows that the boiled enzyme solution contains certain substances which act as catalysts. They catalyze the synthesis of the dextro nitrile as well as the laevo, as the resulting nitrile is always inactive.

The second 50 cc. of the enzyme solution prepared in Experiment 3 was used for a duplicate experiment which was carried out under exactly the same conditions, but was stopped at the end of an hour and a half and the nitrile extracted with ether. The ether was boiled off and the nitrile hydrolyzed with strong hydrochloric acid. It had a volume of 25 cc. after hydrolysis and was laevo active 9.05° in a 2 dm. tube at room temperature.

Rosenthaler had found that, if 1 g. of emulsin in 100 cc. of water was treated with 5 g. of benzaldehyde for 2 hours, the resulting emulsin retained its synthetic activity but the hydrolytic property had dropped to half value under the conditions of his experiment. The activity was measured by the optical activity of the nitrile after a definite interval of time. No attention was paid to the rate of reaction or the equilibrium point. We prepared our extract as in the previous experiment, then to 100 cc. we added 5 g. of our pure benzaldehyde in a glass-stoppered bottle just large enough for the experiment. It was put into a shaking machine and rotated for 2 hours. The enzyme was precipitated with 250 cc. of acetone, then filtered out and washed with alcohol and ether. It was dissolved and made up to 100 cc. in the usual way, half of it being used to study the rate of reaction and get the equilibrium point and the other half to get the optical activity of the nitrile. The second experiment was stopped at the end of one and one-half hours. The nitrile was extracted and hydrolyzed with hydrochloric acid. It had a volume of 25 cc. and was laevo active 9.30° in a 2 dm. tube at the room temperature. Benzaldehyde has, therefore, no deteriorating effect on oxynitrilase so far as its synthetic action goes.

Rosenthaler also found that hydrocyanic acid partly destroyed the hydrolytic power of emulsin on mandelonitrile but had no effect on its synthesis. He treated 1 g. of emulsin with 1.35 g. of hydrocyanic acid in 100 cc. of water for 2 hours. We used 120 cc. of water containing the same concentration of hydrocyanic acid (1.35%) for the extraction of 5 g. of peach leaves for 3 hours. The enzyme was precipitated and re-dissolved in the usual way. Half of it was used to study the rate of reaction and the equilibrium point. The results are given in Expt. 6 in Table I. The second half was used to determine the activity of the nitrile produced. After hydrolysis the volume of the solution was 25 cc. and it read 8.85° laevo in a 2 dm. tube at the room temperature.

The above series of experiments were repeated on the hydrolysis of the nitrile. Unfortunately, we did not succeed in preparing this substance

in the pure state, as we have already said. The samples we bought were even worse than our own, so we used the best we had. This nitrile dissociated so slowly in water that no perceptible change was noticeable after several hours. The blank experiment was carried out as follows: 196 cc. of water and 2 cc. (2.121 g.) of nitrile were put into the wide-mouth bottle, placed in the water bath at 25° and stirred for 30 minutes in order to get the solution saturated with nitrile. 3 cc. of 0.01 *N* alkali was then added and rate of dissociating followed by pipeting out definite amounts at various intervals of time.

TABLE III.

	5 min.	15 min.	30 min.	45 min.	1 1/2 hrs.	1 3/4 hrs.	4 hrs.	20 hrs.	44 hrs.
1. Blank	1.56	2.25	..	3.15	3.66	..	5.30	6.42	6.1
2. Precipitated enzyme	3.66	4.42	..	6.14	..	6.22	..	6.22	6.2
3. Enzyme treated with HCN ...	3.91	4.94	..	6.09	..	6.29	..	6.42	6.4
4. Enzyme treated with benzaldehyde.....	3.77	4.68	5.96	6.09	..	6.32	6.3

The enzyme preparations for Experiments 2, 3, and 4 in Table III were prepared in the same way as for the Experiments 2, 5, and 6 in Table I. In these experiments, the 50 cc. enzyme solution was included in 195 cc. of water which was put into the bottle at the beginning of the experiment. 2 cc. of nitrile was then added and the contents stirred for 30 minutes. Then 3 cc. of 0.01 *N* sodium hydroxide was added and the experiment followed as usual. The figures in the table represent millimoles per liter. A duplicate experiment was carried out to Nos. 2, 3, and 4, which were extracted with ether at the end of 2 hours, after the addition of alkali. The ether was boiled off and the nitrile hydrolyzed. The volume of the hydrolyzed solution was 25 cc. in every case and the activity for the three experiments was $+1.12^{\circ}$, $+1.55^{\circ}$, $+1.6^{\circ}$, respectively, in a 2 dm. tube at the room temperature.

It is apparent from the above results that benzaldehyde and hydrocyanic acid have absolutely no injurious effect on the hydrolytic power of oxynitrilase as the rate of reaction and equilibrium point are exactly the same in every case. The amount of active nitrile is even slightly higher where the enzyme was treated with aldehyde and hydrocyanic acid than where it was not.

We do not consider that Rosenthaler's method is very well adapted for the study of hydrolysis. He suspends the nitrile in water and passes a current of air through the suspension, extracting whatever nitrile is left at the end of 24 hours. It is very likely that he does not actually arrest the reaction at the same point as the amount of nitrile may easily be a variable quantity when the current of air is not actually measured in each experiment. It is also evident that more or less of the benzaldehyde formed is oxidized to benzoic acid which retards the reaction. Con-

quently, one cannot draw any very valid conclusions from his results as he only has one point on the curve.

Rosenthaler has suggested several other methods for separating the synthetic from the hydrolytic enzyme; for example, by treating emulsin with acid and then neutralizing with alkali, by partial precipitation with ammonium sulfate and copper sulfate. We have repeated some of these experiments but we cannot interpret the results correctly until we have made a further study of the effect of inorganic salts on the rate of reaction. There is, however, no evidence of a change in the equilibrium point though there is a marked change in the rate of the reaction.

Conclusions.

1. It is necessary to prepare a stock of pure benzaldehyde and to keep it over nitrogen in order to obtain comparable results in the synthesis of mandelonitrile.

2. There is no evidence of a variation in the equilibrium point in the synthesis of mandelonitrile, even though the oxynitrilase is obtained from widely diversified sources.

3. As far as investigated, there is no evidence of the possible separation of a hydrolytic from a synthetic enzyme in a preparation of oxynitrilase when treated according to methods suggested by Rosenthaler.

We are continuing the study of the general properties of oxynitrilase and expect to repeat all the other methods suggested by Rosenthaler for the separation of the hydrolytic from the synthetic enzyme.

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[FROM THE LABORATORY OF THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL, AND
THE RESEARCH LABORATORY OF ARMOUR AND COMPANY.]

ON THE REACTION OF THE PANCREAS.

By J. H. LONG AND F. FENGER.

Received July 26, 1915.

It is well recognized that the so-called pancreatic juice has a distinct alkaline reaction which has been expressed in different terms. The degree of alkalinity varies with the condition of the alimentary tract with reference to presence of food and with other factors as well. With lowered food ingestion the alkalinity decreases, as has been shown by the investigations of Glaessner,¹ Schumm² and others. The latter found the reaction of the human pancreatic juice from a temporary fistula to be equivalent, in the mean, to about 0.6% Na₂CO₃. The alkalinity found by Glaessner was, apparently, much less, and similar values have been reported by Ellinger and Cohn.³ Observations made by Wohlgemuth⁴

¹ *Z. physiol. Chem.*, 40, 465.

² *Ibid.*, 36, 292.

³ Ellinger and Cohn, *Z. physiol. Chem.*, 45, 28.

⁴ Wohlgemuth, *Biochem. Ztschr.*, 39, 302.

on the flow from a pancreatic fistula gave a degree of alkalinity approximately that reported by Schumm. All authorities agree that the human pancreatic juice is distinctly or even strongly alkaline. In experiments on the reaction of the juice from a fistula made on a dog Auerbach and Pick¹ found the *true* alkalinity, as measured by the potential method, relatively lower than for the human juice. They suggest that the reaction of the liquid which has not lost carbonic acid may be approximately neutral. By the use of the potential method Foa² has found the juice from a dog to be slightly alkaline. In the mean the hydrogen concentration was about $C_H = 0.0085 \times 10^{-7}$.

All investigations thus far available have dealt with a *secretion*, usually secured by aid of a temporary or permanent fistula. The reaction thus found is not necessarily that of the organ itself or the press juice from it. We have thought it worth while to determine the nature of the reaction in the fluid pressed out from the pancreas, or other organ, and believe that some results on the pancreatic fluids of several animals will be reported. The water content of this organ is about 75%, in the mean, but most of this can be separated only by a drying operation, since the cells hold the water very tenaciously.

When the fresh pancreas of the steer, hog or sheep is removed from the body immediately after death, cut open and tested with fresh litmus paper, a well-defined acid reaction is always observed. This is the case no matter how quickly the test is made, and even before the organ is moved, and it persists after the latter has been chilled. It appears to be normal.

We attempted to press out the liquid from the minced glands by the aid of a powerful laboratory press, but the product so secured was not clear and at best was more like a fine emulsion. In some trials the glands were ground up with sharp sand so as to more thoroughly disrupt the cell walls, but the results were unsatisfactory. Finally, it was found that a very good separation could be obtained by centrifugal action. Portions of the minced glands of about 75 g. each were packed in the large tubes of the high power machine employed, four or eight of these tubes being placed in the centrifuge at one time. By rotating at a speed of about 3000 revolutions per minute through 45 minutes the contents of each tube separated into three clearly defined layers, in this order; below a solid layer making up about 50% of the whole, above this a more or less red liquid layer, often quite clear, and making often as much as 25% of the whole contents, and finally a top layer containing much fatty material along with part of the protein tissue of the gland. In amount this

¹ *Chem. Zentr.*, 1, 444 (1913).

² Foa, *Arch. di fisiol.*, 3, 390 (1906); through Neuberg's Handbook, II.

was sometimes in excess of the middle watery layer, and sometimes less. After removing the tubes from the centrifuge and chilling them in ice water it was found possible to separate the liquid layer from the other layers very completely. On filtration this liquid was secured in bright, clear condition. Some investigations as to the nature of the ferment activity in the three layers along with approximate composition are in progress, but in this place the question of the reaction of the liquid layer alone concerns us.

As the filtered liquid always possessed a more or less reddish or yellowish red color it was not possible to measure the reaction by one of the indicator methods. Besides, the protein content was high in most of the juices and this, also, would have added to the uncertainty of the indicator action. As it is possible to secure plenty of the separated juice the potential method of measurement was found to offer the easiest solution of the problem, and in the work we employed Hasselbalch cells along with a calomel electrode maintaining a temperature of 20° as nearly as possible throughout the observations. The cells used were frequently controlled by aid of phosphate mixtures of known potential value. With a mixture of equal volumes of Soerensen's primary and secondary phosphates we found P_H values amounting to 6.803, in the mean. For different cells the extreme values were 6.784 and 6.822. Occasionally two hydrogen electrodes were employed for comparison but work with the $N/10$ calomel electrode gave the most satisfactory control. For work at 20° we used the reduction formula

$$P_H = \frac{\pi - 0.3379}{0.0582}.$$

Observations have been carried out on liquids from beef, hog and sheep pancreases, the glands being removed immediately from the slaughtered animals and worked up without delay. No time was given for any ferment or other change as the centrifuge separation and the potential measurements were carried out within an hour or two after death of the animal. It was found, however, that the potential remained constant through many hours in the cell, in fact over night in some trials made. This is a consideration with some bearing on the explanation of the reaction, as we believe we observe here the true normal reaction of the organ.

Beef Pancreas Juices.

Samples were secured and examined on the dates given below. It is possible that a seasonal variation may be found in the examination of pancreases of animals slaughtered in the winter, and such a test we have in mind. The filtered juices in all these cases remained perfectly clear during the tests, although they occasionally deposited a protein precipitate later, which precipitate is soluble in weak salt solution.

Date.	PH.	CH.
June 11	5.525	29.8×10^{-7}
17	5.469	33.9
18	5.451	35.4
23	5.578	26.4
29	5.602	25.0
30	5.597	25.3
Mean, 5.537		29.3×10^{-7}

Hog Pancreas Juices.

These resemble the beef juices in most respects, but are lighter in color. The same difference shows in the minced glands and, but not distinctly, in the whole glands. Collections and tests were made on the following dates:

Date.	PH.	CH.
June 10	5.609	24.6×10^{-7}
11	5.548	28.3
17	5.447	35.7
18	5.489	32.4
23	5.595	25.4
29	5.574	26.7
30	5.552	28.1
July 6	5.530	29.5
7	5.524	29.9
Mean, 5.541		28.9×10^{-7}

It is plain that the hydrogen concentration values for the two types of pancreases are nearly constant and about the same for the two animals. We have reason for believing that the values for PH on June 17th and 18th are a little low for both sets of observations, because of a slight error in the potential reading which was not recognized until too late to make a proper correction. We are certain that with this correction the results would be much like the others for these days. In digestive activity, however, and other properties the two kinds of glands show no similarity.

Sheep Pancreas Juices.

The digestive activity of the pancreas of the sheep has been but little investigated, and in our experiments we have found the action on starch rather weak. The tryptic power appears to be stronger. No commercial use is made of these pancreases. The juice pressed out or separated by a centrifuge is in general higher in color than was found for the other glands, and appears to be richer in solids. For this reason the preparation of a clear liquid is attended with greater difficulties, and the potential tests must be made with greater dispatch because of the rather rapid separation of a protein precipitate. We add a few results obtained from this type of juice.

Date.	PH.	CH.
July 6	3.575	26.6×10^{-8}
7	5.913	12.2×10^{-7}
14	5.602	25.0×10^{-7}
14	5.623	23.8×10^{-7}
27	5.976	10.5×10^{-7}
27	5.976	10.5×10^{-7}

In these few liquids the hydrogen concentrations are not as regular as in the cases of the hog and beef. For two of the dates the values are approximately the same as found for the other juices, but the sample of July 6th shows a high acidity. In this case very little fat was present and in some other points the behavior was abnormal. The liquid was not clear as in the other juices examined, and this may have had a bearing on the result. The two juices secured on July 14th are much alike and were obtained in perfectly clear condition. These resemblances to the hog and beef juices are very striking. The two juices of July 27th are from young lambs, and while they are practically identical in freezing point, -1.14 and -1.15 , and in acidity, they differ slightly from the earlier samples. But all of the acidities, excepting the first, are of the same order, and are probably related to the blood in the same general manner.

In the centrifugal separation of these fluids some temperature is developed in the machine because of the very high speed of rotation. Care must be observed to keep this down by frequent opening of the centrifuge, to avoid an alteration in the digestive power of the fluids or a possible change in their composition. In the preparation of muscular juices for study Fletcher and Hopkins¹ have observed that the acidity varies greatly with the process followed in grinding the pulp and especially by the temperature obtaining. In this case the acid developed is largely lactic acid, and while the situation is quite distinct from that in our liquid, it is to be recognized that the temperature *might* be a factor. The fact of the rather marked constancy in the results speaks against any very appreciable heat effect. In any event the temperature should not be allowed to go above the normal body temperature.

The acid reaction of the pancreas is undoubtedly the normal one, and it has been overlooked because the duct flow from a fistula is so plainly alkaline. This reaction is what should be expected when it is recalled that the source of both liquids is the nearly neutral blood with its high content of primary and secondary phosphates. In the normal activity of the gland the work of the cells results in sending an excess of one phosphate to the intestine while an excess of the other is retained to make the gland tissue slightly acid. We find that this acid liquid is very rich in acid phosphate, while the ordinary pancreatic juice contains an excess of the secondary phosphate, which is partly responsible for the reaction

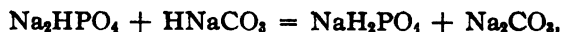
¹ *J. Physiol.*, 35, 247.

usually ascribed to carbonates. The amount of carbonate in the press juice is small.

Similar liquids may be separated from other organs and the reaction is frequently acid. This we have found in the liver. The bile from the liver is commonly spoken of as alkaline but this is not always the case, and perhaps not normally. Much depends on the age of the examined bile as far as the reaction is concerned, and the fresh bile is nearly neutral or even acid, when examined by the potential method. We are making a more thorough study of the reactions of a number of the fluids which may be separated from various organs by the centrifugal method.

The normal blood reaction is approximately $P_H = 7.52$, which may be easily duplicated by proper mixtures of primary and secondary phosphate, or by combination of these with sodium bicarbonate, as shown especially by L. J. Henderson.¹ With a mixture of about 8.5 volumes of molec./15 secondary phosphate with 1.5 volume of primary phosphate of the same concentration we have approximately the blood reaction, while 9 volumes of the primary phosphate and 1 volume of the secondary phosphate, each of the molec./15 concentration, gives about the reaction we find in the liquids from the pancreases. A reversal of these last proportions furnishes a reaction such as we sometimes find in the fistula juices. It is evident that a change in the proportions in which the two phosphates are mixed would account for the various degrees of acidity or alkalinity we note in the two kinds of pancreas liquids.

A selective secretion from a mixture of secondary phosphate and bicarbonate would lead to the difference in reaction observed between the liquid retained and that excreted by the pancreas. The reaction of the fistula juice is that of a normal carbonate, rather than bicarbonate, which may be accounted for through the cell activity working in this manner.



the primary phosphate resulting being more largely retained within the organ while the carbonate is thrown to the duct or fistula. The freshly cut surface of the pancreas, or the separated liquid, will usually liberate carbon dioxide from solution of bicarbonate added, just as we have liberation of the gas when we mix properly diluted solutions of bicarbonate and primary phosphate. The centrifugal liquid yields 1.5% or more ash, over half of which is in the form of P_2O_5 , and this phosphoric acid content is apparently nearly constant in the various juices examined. The matter will be discussed elsewhere, as will also the general question of the composition of the several fractions referred to above, and the behavior. It may be remarked here that a very sharp amylolytic activity was found in the liquid fraction, as well as characteristic tryptic

¹ *Ergebnisse der Physiol.*, 8, 254.

behavior, without the addition of any form of activator. The minced gland itself furnishes all that is necessary to activate the trypsinogen.

Conclusions.

We have shown that it is possible to separate the true press juice from the minced pancreas, and best by aid of a powerful centrifuge operating at a speed of 3000 revolutions, or over, per minute. In the centrifugal separation the minced mass divides into three layers of distinct properties. The lower layer is largely protein, the middle layer a clear liquid, and the upper layer solid with much fat present.

The liquid layer has a marked acid reaction, as distinct from that of the so-called pancreatic juice, which reaction is nearly a constant for beef and hog glands. The juice is rich in phosphates and the reaction seems to be due to acid phosphate. This reaction may be as constant and characteristic as is that of the blood and may be expressed, approximately, by the relation,

$$C_H = 29 \times 10^{-7}.$$

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE LABORATORY OF SOIL CHEMISTRY OF THE IOWA STATE COLLEGE EXPERIMENT STATION.]

AMINO-ACID NITROGEN OF SOIL AND THE CHEMICAL GROUPS OF AMINO ACIDS IN THE HYDROLYZED SOIL AND THEIR HUMIC ACIDS.

By R. S. POTTER AND R. S. SNYDER.

Received July 6, 1915.

This investigation was undertaken to correlate, if possible, the amounts of the various chemical groups¹ (1) in the soil with its humic acid, (2) in the soil and its humic acid with the kind of organic fertilizer previously applied to the soil, (3) in the soil and its humic acid with similar groups found in pure proteins, and (4) to compare the amounts of amino acid nitrogen, as such, in the soil with that found by hydrolysis. No study of just this nature has ever been made. Several investigators, in recent years, subjected the solution obtained by boiling the soil with strong acids to the Osborne and Harris-Hausmann method. Kelley and Thompson² analyzed the alkali extract and the humic acids of several soils by this same method.

Suzuki³ analyzed three humic acids rather extensively. Humic acid A was a Merck product, origin unknown to Suzuki. Humic acids B and C were prepared, respectively, from an unmanured soil and a compost

¹ Van Slyke, *J. Biol. Chem.*, 10, 15 (1910).

² *THIS JOURNAL*, 36, 438 (1914).

³ *Bull. Col. Tokyo*, 7, 513 (1907).

heap. Each acid was boiled for ten hours with strong hydrochloric acid. Besides other determinations, the amount dissolved, the amide, basic and nonbasic nitrogen were determined. 65-75% of the total nitrogen was dissolved by the acid, and in the extract 41-62% of the nitrogen was not precipitable with phosphotungstic acid. A large sample of the humic acid A was then hydrolyzed and the quantitative separation of the amino acids by the Fisher method¹ carried out. Small amounts of most of the protein amino acids were obtained. This work showed that at least part of the humic acid was of a protein nature. It is unfortunate that the origin of the acid was unknown to Suzuki. He states that, according to its general behavior, it probably was prepared from peat.

Since about half of the experimental work in connection with this investigation was completed, a paper has appeared by Lathrop² in which he gives analysis of "base goods" fertilizer by the Van Slyke method. The comparison of our results with those obtained by him will be of some interest and will be taken up in the experimental part of this paper.

The soils used in this work were obtained from experimental plots maintained by this Station and are located on the Wisconsin drift area. They consist of 1/20 acre plots situated side by side and separated by four foot alleys and are numbered 101 to 114. In this work soil from 101, 102, 103, 104, 106, 107, and 108 was used. There is a slight slope from plot 114 to 101. Previous to 1907 inclusively, the soils had received the ordinary farm cultivation. Since that time the soils used by us have received the following treatments:

Plot.	Cultivation.	Treatment per acre.
101.....	Timothy annually	Nothing added
102.....	Fallowed	2 T. peat annually
103.....	Fallowed	8 T. manure 1909-1913
104.....	Fallowed	8 T. clover 1909-1913
106.....	Fallowed	2 T. timothy annually
107.....	Fallowed	Nothing
108.....	Fallowed	2 T. oat straw annually

In addition to these soils a peat soil taken from one of the Station pastures was used. The soils were all collected during the winter of 1914-1915, immediately air dried and ground. In order to render the humus more soluble the soils were all extracted with 1% hydrochloric acid in the usual manner.

In Table I are given the amounts of nitrogen extracted by the acid, together with the total nitrogen of the soil.

¹ *Z. physiol. Chem.*, 33, 151, 412 (1901).

² *J. Ind. Eng. Chem.*, 7, 228 (1915).

TABLE I.

Soil.	Total nitrogen in per cent.	Nitrogen extracted by 1% HCl.	
		In per cent. of soil.	In per cent. of total N.
101.....	0.306	0.00490	1.60
102.....	0.336	0.00406	1.23
103.....	0.300	0.00546	1.82
104.....	0.270	0.00392	1.42
106.....	0.245	0.00406	1.66
107.....	1.234	0.00532	2.27
108.....	0.224	0.00504	2.27
Peat.....	1.770	0.01191	0.673

In considering the total nitrogen values, it must be remembered that there is a gentle slope down to plot 101 and hence there is a tendency for these plots to contain more nitrogen than those higher up. In the case of the results for the amount of nitrogen extracted by the 1% acid, the differences are not marked. Both the peat and the peat treated soil being low, shows that the peat has not lost its character after entrance to the soil.

The soils were in all cases hydrolyzed in the same way, namely, by boiling one part of soil with two parts of 22% hydrochloric acid for 48 hours. At the end of this period the mixture was allowed to cool somewhat, filtered and washed until free from chlorides. The filtrate, combined with the wash water, was evaporated to about 200 cc., made up to exactly 250 cc., and two 25 cc. portions were taken for analysis for total nitrogen. The 200 cc. remaining were divided into two portions of 100 cc. and the Van Slyke method, exactly as outlined by the originator, was applied to each portion. Cystin nitrogen was analyzed for in the case of two soils, but only a questionable trace was found in each case, so that for the remaining soils this determination was omitted. No doubt the cystin was decomposed by the long treatment with the acid.

It is not thought that the nitrogen as found by the Van Slyke method, working with such a complex as the soil, is in reality, all lysine, histidine, etc., nitrogen. It might be said that each group, as found, represents a class of compounds having the particular reaction by which the lysine, histidine, etc., nitrogen, respectively are determined. For extraction we have arbitrarily shaken 25 g. samples of the soils with 100 cc. of 1% sodium hydroxide for five hours. The mixture was then centrifuged in a high speed machine.¹

Most investigators, in preparing humic acids have precipitated the humus solutions by slight acidification with one of the mineral acids, but, as has been shown by Shorey,² upon neutralizing the filtrate from the humic acids another precipitate is given which contains nitrogen. This

¹ For description see *Iowa Sta. Bull.*, No. 124 (1911).

² U. S. Dept. Agr., *Hawaii Sta. Rept.*, 1906, p. 51.

is to be expected if the humus solution contains any protein material. In view of this and because of the rather general use of dilute acetic acid as a protein precipitant, it was decided to try the use of this reagent. Table II gives the results of some preliminary tests. One per cent. sodium hydroxide was the extractive reagent throughout. Twenty cc. portions were carefully neutralized with sulfuric acid and then sufficient 10% acetic acid added to give the desired strength. The mixture was heated at the boiling point for 15 minutes and then filtered by suction through paper pulp, and the precipitate washed with the same strength acid as the solution from which it had originated.

TABLE II.

Soil.	A.			103.			107.		
Strength acetic acid (%).....	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Nitr. ppt. in % total N.....	63.7	55.6	55.0	73.7	70.0	68.1	87.0	83.4	81.3

While it is possible that a weaker acid might have precipitated a greater amount of nitrogen, it was found to be extremely difficult to filter such a mixture.

The humic acids used in the subsequent analysis were prepared as follows: 150 g. of the acid extracted soil were placed in an 800 cc. bottle and shaken 5 hours with 1% sodium hydroxide and then immediately centrifuged. Precautions were taken to keep the loss of ammonia as low as possible. The extract so obtained was very carefully neutralized to litmus with sulfuric acid and then sufficient strong acetic acid to give a 0.5% solution was added. The mixture was heated at the boiling point for 15 minutes, and filtered by suction on a Buechner funnel containing two thicknesses of a good filter paper. After filtration the precipitate was transferred to a flask, 22% hydrochloric added and then the mixture was hydrolyzed for 48 hours. In some cases it was found to be impossible to transfer the humic acid to the flasks quantitatively. Where this was the case the procedure was as follows: A small portion of the alkali extract, usually 250 cc. was carried through the regular procedure, it always being possible to work quantitatively with such an amount. The hydrolysis was carried out and the humin and amide nitrogen determined. From the data so obtained the amount of extract in the larger sample was calculated.

After the completion of the hydrolysis the mixture was filtered and the undissolved residue washed free from chlorides. The residue was analyzed for total nitrogen. The filtrate was concentrated to about 200 cc., made up to exactly 250 cc., and two 25 cc. portions were taken for analysis of total nitrogen. The remaining 200 cc. were used for the determination of the chemical groups according to Van Slyke, in the case of soils 102, 103, 106, and 107 dividing it into two portions and carrying the analysis

out in duplicate. With the other soils the whole of the 200 cc. portion was used for one analysis. The precipitate found with the lime was analyzed for total nitrogen and to this was added the nitrogen from the insoluble residue, and the sum called humin nitrogen.

TABLE III.

Soil.	Extraction reagent.	Amide.	Melamin.	Arginine.	Histidine.	Lysine.
101.....	22% HCl	24.09	6.68	4.03	4.23	2.25
	1% NaOH	7.49	9.94	1.85	1.76	0.43
102.....	22% HCl	25.61	8.65	5.08	3.41	2.74
	1% NaOH	5.14	9.25	0.80	1.06	0.70
103.....	22% HCl	23.0	6.68	3.55	1.99	1.69
	1% NaOH	5.66	5.03	0.64	0.65	0.54
104.....	22% HCl	23.38	7.45	3.92	2.78	1.29
	1% NaOH	9.48	21.5	1.83	1.54	0.75
106.....	22% HCl	27.21	8.60	4.83	3.47	3.22
	1% NaOH	4.83	6.62	0.93	1.06	0.43
107.....	22% HCl	27.20	8.35	4.34	3.91	2.46
	1% NaOH	8.88	12.46	0.87	0.65	0.66
108.....	22% HCl	26.64	8.72	4.66	6.30	1.82
	1% NaOH	10.0	14.07	2.68	2.91	0.82
Peat.....	22% HCl	18.36	5.95	3.72	2.03	2.95
	1% NaOH	2.54	1.33	0.38	0.21	0.19

Soil.	Total basic.	Monoamino.	Nonamino.	Total nitrogen found.	Extracted.	Humic acid.
101.....	10.51	26.17	5.41	72.86	74.02	...
	4.05	7.34	2.95	31.77	42.0	32.1
102.....	11.23	24.62	3.85	73.96	75.12	...
	2.56	7.45	0.92	25.32	41.9	25.7
103.....	7.23	28.11	2.40	67.42	70.93	...
	1.83	6.72	1.15	20.39	28.6	21.0
104.....	7.99	27.21	5.00	71.03	74.31	...
	4.12	9.36	0.94	45.4	53.1	46.8
106.....	11.52	21.28	4.46	73.07	76.47	...
	2.42	5.54	1.68	21.1	31.8	21.0
107.....	10.71	21.01	3.91	71.18	71.31	...
	2.18	7.22	0.96	31.7	36.8	31.7
108.....	12.78	25.22	2.11	65.47	68.68	...
	6.41	9.80	1.0	41.28	52.2	43.0
Peat.....	8.70	31.72	6.15	70.88	71.37	...
	0.78	1.85	0.37	6.74	8.42	6.61

The results, together with those found by the analysis of the hydrochloric acid extract, are given in Table III, and are all expressed in per cent. of total soil nitrogen.

The results in Table III will be discussed only quite briefly. The amounts of nitrogen extracted by the strong acid are fairly constant; that extracted by the weak alkali varies widely and the variations are of no apparent significance. The amount of humic acid in the various soils is quite different. Whether this is due to some other differences, perhaps

physical, it is not possible to state. It is also possible that the use of such a small amount of weak alkali, relative to the amount of soil, used might have caused the differences. It was noticed that it required quite different amounts of sulfuric acid to neutralize the alkali extract for the different soils.

The most significant thing brought out by the table is the high amounts of humin nitrogen in the humic acids. Insofar as humin compounds are a sharply defined class of compounds it is hardly probable that all our humin belongs to it. Yet our material possessed many of the properties of this class of compounds. It was black, insoluble in all the organic solvents, dilute acids, salt solutions, and soluble in dilute alkali. In this connection a recent paper by Gartner and Blish¹ is of interest. Working with pure zein and gliadin they showed that the humin compounds had their origin in tryptophane, and that, contrary to the rather general belief, nitrogenous humins are not formed by the "adsorption of ammonia by nonnitrogenous humins formed from carbohydrates." In the soil there is, of course, carbohydrate material and it would seem that the amount of humin found by use would be too large to all come from the tryptophane. However, it may be that it is possible for other substances containing the NH group to form humin. The above investigators found that histidine did not form humin. In the continual degradation of the soil organic matter there would be a natural tendency for the humin to accumulate for, of course, this material once formed would be very resistant to further change.

The amounts of humin nitrogen found in the hydrochloric acid extracts is probably of no significance, for the amount found varied with the number of times the soil residue was washed. As long as there was any acid left the wash-water was clear, but towards the end of the washing brownish material was taken out, due no doubt to a passing over to the colloidal state. This brown material carried a great deal of nitrogen with it.

Because of the varying and abnormally high amounts of humin nitrogen in the acid extract and in the humic acids, for the purposes of better comparison the results have been calculated on the basis that amide + basic + monoamino + nonamino = 100. This will permit of the more active groups being compared. The calculation is found in Table IV. In the same table the results, calculated to the same basis, for four proteins are given. These values are taken from Van Slyke.²

The most noteworthy thing brought out by the comparison of the values for the soil and the proteins is the highness of the values for the amide nitrogen, and the lowness of the basic and nonbasic nitrogen. It

¹ THIS JOURNAL, 37, 1630 (1915).

² *Loc. cit.*

is a somewhat general property of the vegetable proteins to yield high amounts of amide nitrogen but none so far examined have given more than gliadin. It is rather surprising that soil should have such a relatively high content of amide nitrogen, as it is the nitrogen of this group which is the most quickly hydrolyzed upon boiling proteins with acids. One would think that the organic matter in soil which has been subjected to an extended period of decay, would be rather deficient in this group. Perhaps the synthetical operations more than overbalance the decomposition. In this connection it would be interesting to have some data on the nitrogen distribution of the bacterial proteins, but so far as we know no such data is to be had at present.

TABLE IV.

Soil.	Material.	Amide.	Arginine.	Histi- dine.	Lysine.	Total basic.	Mono- amino.	Non- amino.
101.....	HCl ext.	36.4	6.08	6.40	3.40	15.9	39.0	8.7
	Humic acid	34.2	8.50	8.08	1.99	18.6	33.8	13.4
102.....	HCl ext.	39.2	7.78	5.22	4.20	17.2	37.7	5.32
	Humic acid	32.0	4.92	6.59	4.34	15.9	46.4	5.8
103.....	HCl ext.	37.8	5.83	3.28	2.77	11.89	46.2	4.11
	Humic acid	36.9	4.18	4.21	3.50	11.9	43.7	7.5
104.....	HCl ext.	36.8	6.18	4.37	2.02	12.9	42.8	7.9
	Humic acid	39.6	7.65	6.45	3.16	17.3	39.2	3.9
106.....	HCl ext.	42.2	7.50	5.38	4.99	17.85	33.0	6.9
	Humic acid	33.4	6.39	7.30	2.97	16.7	38.3	11.6
107.....	HCl ext.	43.3	6.90	6.22	3.92	17.0	33.4	6.2
	Humic acid	46.2	4.54	3.41	3.43	11.4	37.6	4.95
108.....	HCl ext.	39.9	6.97	9.44	2.74	19.15	37.8	3.15
	Humic acid	36.8	9.88	10.70	3.02	23.5	36.0	3.7
Peat.....	HCl ext.	28.3	5.72	3.13	4.56	13.4	48.8	9.45
	Humic acid	46.6	7.04	3.83	3.48	14.3	34.2	5.0
	Gliadin	25.5	5.77	5.26	0.76	13.05	52.5	8.6
	Edestin	10.18	27.8	5.90	3.97	39.2	48.8	1.75
	Fibrin	8.63	14.4	5.01	11.95	32.3	56.3	2.8
	Hemoglobin	5.44	7.98	13.2	11.3	32.5	59.1	3.0

On comparing the relative proportions of the various groups in the acid extract and the humic acids there are no noteworthy differences. In fact, with few exceptions there is a rather surprising similarity. To us it means that the organic matter extracted by alkali is of no very different character than the organic matter of the soils as a whole. This, together with the fact proved by Fraps and Hammer¹ that, upon adding organic matter to soil, at the end of a year's time there is no more material extracted with dilute ammonia than at the beginning of the period, proves quite conclusively that the determination of the amount of humus as found by the various methods is of no particular value in the study of a soil.

Nothing very significant can be deduced from the variations in the

¹ *Tex. Bull.*, 129 (1910).

different soils. The treatments have not been continued for long enough time to change materially the character of the original organic matter. Since these plots are a permanent feature of this Station it is hoped that similar analyses in after years will throw more light on the subject.

As to the question—just what is the constitution of humic acid? The idea that humic acid is a definite compound or even the mixture of a few compounds has been exploded long ago. According to the investigations of Suzuki, Kelley and the data here presented it contains material of a protein nature. Weak alkali solutions extract more protein material from seeds than any other extracting reagents and, according to Osborne,¹ usually in an unaltered condition. The form they are in when precipitated with acids depends upon the amount of acid added. In the soil, where there is undoubtedly a comparatively high content of dead bacterial cells, which would contain relatively high amounts of nucleoproteins, it would seem that part of the precipitate obtained on adding acid to the alkali extract would be made up of combinations of protein material with nucleic acid² as well as other organic acids. Of course the protein might also be precipitated unchanged or as a salt of the acid used for precipitating it.

The free amino acid and the peptide nitrogen in the unhydrolyzed soil was determined by the Kober method³ as we have applied it to soils. These results, which are given in Table V, are interesting in that they show how small the amount of amino acid and peptide nitrogen is in comparison to that present in the organic matter after hydrolysis. Lathrop,⁴ in the discussion of his results on the "base goods" fertilizer, seems to hold that such compounds as histidine would be of direct significance in plant nutrition especially when added to the soil in the "base goods." In view of the fact that the amino acid nitrogen in all soils examined by us is so small makes such a possibility seem quite remote to us. These compounds would probably be adsorbed to an extent at least as great as ammonia, so that they would be present in the soil solution in but the merest traces. The recent work of Upson and Powell,⁵ shows that many compounds, quite toxic to plants growing in water culture, are not at all or at most only slightly toxic when used in soil culture. It evidently is the investigator's intention to extend their experiments, and the results for the beneficial compounds will be awaited with interest.

¹ "The Vegetable Proteins," 1912, p. 18.

² Nucleic acid was found in many soils by Shorey, U. S. Dept. Agr., Bureau of Soils, *Bull.*, 88 (1913).

³ *THIS JOURNAL*, 35, 1546 (1913).

⁴ To appear shortly in the *J. Ind. Eng. Chem.*

⁵ *Loc. cit.*

⁶ *J. Ind. Eng. Chem.*, 7, 420 (1915).

TABLE V.

Soil.	Free amido acid nitrogen.	Polypep- tide ni- trogen.	Soil.	Free amino acid nitrogen.	Polypep- tide ni- trogen.	Soil.	Free amino acid nitrogen.	Polypep- tide ni- trogen.
101	0.30	0.56	104	0.40	0.92	108	0.65	1.50
102	0.29	0.88	106	0.24	0.74	Peat	0.071	0.26
103	0.16	0.84	107	0.29	0.71			

Conclusions.

1. The amount of nitrogen precipitated from a neutralized alkali extract of soil varies, in a qualitative way, inversely with the strength of the acid.

2. The amount of humin nitrogen, as found by the Van Slyke method, extracted by dilute alkali from soil is very high when compared to the amounts in proteins.

3. Dilute alkali does not extract any typical class of organic compound from the soil.

4. Before definite conclusions are drawn from the remainder of the Van Slyke results it is believed that analyses on these same plots in future years should be awaited.

5. The amount of amino acid and peptide nitrogen in soil is found to be very small when compared to the amounts of amino acids formed by hydrolysis.

AMES, IOWA.

[CONTRIBUTION FROM THE HARE CHEMICAL LABORATORY, UNIVERSITY OF PENNSYLVANIA AND LABORATORY OF PHYSIOLOGICAL CHEMISTRY, COLLEGE OF MEDICINE, UNIVERSITY OF ILLINOIS.]

A DISTURBING FACTOR IN BARFOED'S TEST.¹

BY WILLIAM H. WELKER.

Received July, 1915.

Barfoed's test has been used extensively in biological chemistry for the detection of reducing monosaccharides. In this connection, it was used to show the difference in the chemical reaction between starch paste and hydrolytic products obtained from starch paste by boiling with dilute hydrochloric acid. It was found that when starch could no longer be detected with iodine it was impossible to obtain the typical glucose reaction with Barfoed's reagent, but that a greenish white precipitate was formed. All mineral acid had been removed from the solution of the hydrolytic products by neutralization with sodium hydroxide and the solution was subsequently made very faintly acid with acetic acid. These experiments seemed to indicate that sodium chloride was the substance that interfered with the reaction. In order to ascertain whether this

¹ Preliminary communication; *Proc. Am. Soc. Biol. Chem.*, 1909, p. 180. Read before the Medical Research Club, University of Illinois, Chicago, Ill., June 9, 1915.

assumption is correct the following experiments were made: A solution of sodium chloride was boiled with Barfoed's reagent. A greenish white precipitate was formed. When sodium chloride was added to a solution of pure glucose and Barfoed's test was applied to the mixed solution, a greenish white precipitate was formed instead of the red cuprous oxide of the typical Barfoed's test. Since the first part of this work was done, Mathewson,¹ has shown that a great variety of inorganic, as well as organic compounds, interfere with this test.

Interfering Concentration of Sodium Chloride.—A series of tests was made to determine the concentration of sodium chloride which would interfere with the Barfoed's tests in various concentrations of glucose. The tests were carried out as follows: Five cc. of glucose solution, 4 cc. of sodium chloride solution and 1 cc. of Barfoed's reagent were measured into a test tube and the mixed solution was boiled for thirty seconds over a free flame. Table I shows the results of these experiments.

TABLE I.

Percentage concentration of sodium chloride.	Percentage concentration of glucose.					
	0.163.	0.312.	0.625.	1.25.	2.5.	5.
0.0156	Reduction and precipitate					
0.0312						
0.0625		Very faint reduct.				
0.125		Ppt.	Very faint reduct.	Reduct.	Reduct.	Reduct.
0.25			Ppt.			
0.5				Ppt.	Ppt.	Ppt.

In a second series of experiments the same amounts of the various solutions were used as in Table I but instead of heating the mixture over a free flame, it was heated in actively boiling water for two minutes. The results of these experiments are shown in Table II.

Delicacy of Barfoed's Test.

In a series of experiments to determine the delicacy of the reaction, it was found that when the test is performed with 1 cc. of Barfoed's reagent, 9 cc. of glucose solution and the mixture is heated in boiling water for two minutes, a concentration of 0.08% of glucose gives a very definite reduction and half that concentration gives a faint reduction.

The Barfoed's reagent used in this work was made according to the directions of Barfoed² in his original paper. Five cc. of 38% acetic acid were added to 200 cc. of a solution of copper acetate. The copper acetate was made up in the proportion of 1 part of salt to 15 parts of water.

¹ Mathewson, "A Study of Some of the Biochemical Tests," Dissertation, Columbia University, 1912.

² Barfoed, *Z. anal. Chem.*, 12, 27 (1873).

TABLE II.

Percentage conc. of NaCl.	Percentage concentration of glucose.										
	0.05.	0.1.	0.2.	0.4.	0.6.	0.8.	1.	2.	3.	4.	5.
0.01	V. f. r.										
0.02	V. f. p.	V. f. p.; R. F. r.	+++								
0.04			Ppt.								
0.06				F. p.; Marked r.							
0.08				V. f. r.	V. f. r.						
0.1				Ppt.	Ppt.	V. f. p.; R.	V. f. p.; R.	R. ++	R. ++	R. ++	
0.2								Ppt. +++	Ppt. +++	Ppt. ++	F. p.; F. r.
0.3											
0.4											
0.5											

V. f. r. = very faint reduction; V. f. p. = very faint ppt.

Influence of Sodium Chloride at Room Temperature.—A series of experiments was conducted to show what concentration of sodium chloride will cause a precipitate with Barfoed's reagent when allowed to stand at room temperature. The experiments were conducted as follows: Four cc. of sodium chloride solution were mixed with 1 cc. of Barfoed's reagent and the mixture was allowed to stand at room temperature for twenty-four hours. In these experiments a sodium chloride concentration of 0.32% gave a precipitate. With a concentration of 0.16% sodium chloride, no precipitate was formed.

Effect of Glucose on the Formation of the Greenish White Precipitate.—The next series of experiments was undertaken to determine whether glucose had any effect on the formation of this precipitate at room temperature. The volumes of the various solutions used in these experiments were the same as in Table I and II. The results are shown in Table III.

TABLE III.

Percentage concentration of sodium chloride.	Percentage concentration of glucose.				
	0.25.	0.3.	1.0.	2.5.	5.0.
0.1	Opalescence in 15 hours.				
0.2 to 0.9.	Opalescence within two hours in all cases.				
1.0	Marked opalescence within a few minutes.				

Glucose seems to favor the formation of opalescent solutions (colloidal) as indicated by its appearance in a lower sodium chloride concentration than in the experiments without it.

Nature of Greenish White Precipitate.—The greenish white precipitate that is formed, contains copper, sodium, chlorine and the acetic acid

radical. When this compound is allowed to form at room temperature it tends to go into colloidal solution. Boiling hastens the precipitation. The percentage composition of this precipitate has not been determined.

Conclusions.

Under the conditions of these experiments it appears that a very small percentage of sodium chloride interferes with Barfoed's test.

CHICAGO, ILL.



Chas. W. Sherry.

THE JOURNAL

OF THE

American Chemical Society

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American Chemical Journal
(Founded by Ira Remsen)

COÖPERATION IN MATTERS CHEMICAL.¹ PRESIDENTIAL ADDRESS.

BY CHARLES HOLMES HERTY.

The expressive and recently much quoted phrase, "Don't rock the boat," is an injunction promotive of safety, but the closely related "Pull together," of common parlance, suggests the method of effective advance. In the hope, therefore, of aiding somewhat that line of progress in which we feel particular interest and for which we are largely responsible, I have chosen as a subject for this occasion, "Coöperation in Matters Chemical."

Its treatment must necessarily be purely national, for the international aspects have been eliminated by the embitterments of the European struggle. Just three years ago there met together in New York City, on the occasion of the Eighth International Congress of Applied Chemistry, representatives of all the leading nations of the world for report and conference on subjects pertaining to the advance of that science whose interests call us together now. The key-note of that meeting was, "Science knows no geographical boundaries," and plans were enthusiastically formulated for future coöperative effort.

Alas, how unexpectedly, how grievously and how completely that key-note has been forgotten, those plans set aside, amid the strife and tur-

¹ Presidential address, Fifty-first Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915.

moil of war. The words "forgotten" and "set aside" are used advisedly, for that key-note is eternal verity, and men of all nations must work together if the greatest progress is to be realized. The unfortunate re-creminations of men of science, so widely heralded in recent months, will eventually be replaced by those nobler feelings of brotherhood which lie deep in the hearts of all whose life-work has been the search for truth.

Meanwhile, chemistry is suffering a staggering blow; the call for men in European armies has almost depopulated university laboratories, the gripping realities of war have absorbed the thought and interest of many of the leaders of our science, and the shrinkage of many chemical journals, as already evidenced in our own "Chemical Abstracts," bears abundant witness to the lean years that are just before us. That this sterility of production is to be extended far beyond the actual duration of the war period is emphasized by the ages of the men who constitute the bulk of the armies. The loss of such young men, the leaders of the next generation, casts its shadow before.

How does this situation affect us here where the curse of war has not fallen? Surely we would be false to our science, to ourselves and to humanity if we did not strive with redoubled effort to make good this present and oncoming deficiency so far as in our power lies.

It would be a work of supererogation for me to make any plea for research or to attempt its justification before the members of the American Chemical Society; for this organization embraces within its now more than seven thousand members that great body of men whose tireless efforts have within the last two decades so richly increased chemical literature, and the publications of this society show annually increased volume in the preservation and dissemination of the records of such research. The ever-present struggle between the makers of the budget and the pressing claims of the editors of our journals is sufficient proof of the rapid growth of research in America. Happily the day has passed when our chemists felt the need of publication in foreign journals to insure wide hearing. All honor to the men who early determined that America should have publications worthy of the name and who consistently gave their loyal support to this great undertaking!

The aim of research is the discovery of truth. On this point all are agreed. But why such an aim? "Truth for Truth's sake," "Science for Science's sake," and similar familiar phrases have no meaning to me. I can find only one answer to this question—the uplift of humanity. In the engrossing interest of research problems, however, we sometimes adopt an artificial division of scientific research into "pure" and "applied," the former term uttered sometimes by university men in a tone of snobbishness, the latter occasionally by men of the technical labora-

ories with a rather disdainful regard of obligations to the science on which their operations are based.

I think of research in chemistry as a field whose highest fruition calls for two kinds of service. On the one hand the constant enrichment of the soil, "pure chemistry," if you will, and on the other the seeding, tending and harvesting, "applied chemistry;" each absolutely essential, and incapable of its highest fulfillment without the other, using the same methods, demanding identical care, skill, accuracy and thoroughness, and working toward the same end—the uplift of humanity. If this be not the mutual goal, then pure chemistry becomes a selfish toy and applied chemistry a mere tool for greed. In both lines of service the hearty co-operation of all chemists is needed.

The continued use of the terms "pure" and "applied" in what follows involves, therefore, no question of relative dignity or scientific justification, but is based simply on that privilege of convenience which we reserve to ourselves in continuing the use of the terms "organic" and "inorganic" chemistry.

For training in the ideals and methods of chemical research we rightly look to our universities, and if the ideal of research include both "pure" and "applied," then must the universities set forth that ideal both in word and act. Its formal statement, accompanied by discriminating favor toward the one or the other in the actual lines of work pursued, does not meet that full responsibility which every university bears to chemical research.

And this brings the responsibility to the individual laboratory head, for in his own department he represents his university. Whatever his ideal, rest assured it makes its full imprint on those working under him. The joint planning of work, the daily informal conference in the laboratory and mutual presence at the dawn of new truth create naturally in the student a strong bond of sympathy and loyal regard. Ideals are unconsciously absorbed. Thus there are sent forth each year from the laboratories young men impressed with the ideals of the men in charge, and thus is the national viewpoint in such matters largely determined. I speak now of the average American university, fully conscious of the necessity of differentiation of work in the staffs of the larger institutions and equally conscious of the difficulties under which men in the smaller institutions often work. But the ideal holds for one and all alike.

The claims of research in pure chemistry in our universities need no urging on my part. The opportunities and inducements for such work already abundantly exist. It is gratifying to note the change of popular sentiment toward such work. The old question "Of what use?" is grad-

ually being replaced by a sound conception of the fundamental function of the science of chemistry and by a recognition that the advancement of this science is not effected by inspiration, but by the contributions of many zealous, patient and enthusiastic workers. By slow process of accumulation the data are supplied for new generalizations which bring us gradually nearer and nearer full truth.

The record in the Journal of this Society shows a steadily increasing output of such work from university laboratories. That the amount of this work will increase is a hope and a belief fully justified by the attitude of university authorities in providing better laboratory and library facilities and more fellowships for graduate students.

In connection with the subject of university research in pure chemistry, may I be permitted a word concerning a special class—the men in charge of laboratories in smaller institutions of learning. Fresh from doctorate training, they enter upon the new responsibilities filled with zeal and a fine fire for continuation of research. After a period of adjustment to normal duties of the new environment and with thoughts turned to independent research there comes the realization of the poverty of equipment both in laboratory and in library facilities as compared with former surroundings. Then comes a period of earnest effort to better this equipment, only to find how many other undeniable demands are being made on the very limited institutional funds. There follows a period of depression and discouragement, and then—how often that worker is lost to the cause of pure chemistry!

But is the situation really as bad as it sometimes seems? Many of the most valuable researches in the literature have been conducted on inexpensive material and often under most discouraging circumstances. If money is lacking, there are endowment funds to aid research, and, to supplement inadequate library facilities, there is the splendid library service of the United Engineering Society of New York City. By such means it may still be possible to follow that first fine impulse.

The great danger to research in pure chemistry in America at the present time lies in the mental distraction and demoralization resulting from engrossing consideration of daily developments of the European war. The mammoth scale and startling disclosures of that fearful struggle as depicted in the morning, evening and ever appearing "extra" newspapers challenge our constant attention and fill us with the horrors of the situation. Is it right that we give way to this demoralization and thus increase the disastrous effects of such abnormal times?

Chemistry, perhaps more than any other branch of science, has received wide advertisement in connection with the present war. Many

to whom it was formerly little more than a name, have within the past year done it homage; but such glorification has emphasized the application of chemistry rather than the broad, deep foundation which has been so quietly laid by the workers in university laboratories during the years that have passed. Pressure for industrial application of chemistry along very restricted lines is great at present. The public is willing to listen and capital ready to invest. It seems fitting, therefore, that at this moment emphasis be laid on the basic science which underlies these applications. It seeks no advertisement and often in disjointed form receives but scant recognition, but it is the soil from which the fruitage must spring. To the maximum development of that soil all chemists, at least to some degree, are pledged and bounden. I do not hesitate, in a plea for coöperation, to urge that in all industrial research laboratories, ranging from those of the large corporations, splendidly manned and equipped, to those of the youngest analytical chemists, there be carried on some line of research which has no special client, for which no fee is expected, but whose function is to repay in some slight degree the debt that every chemist owes to the science of chemistry. The subjective influence of such work would far more than compensate for the time spent in its execution.

The ideal of research which I am urging includes both pure and applied chemistry. Since it is the function of universities to give the younger generation, chiefly through research, that training which will equip them for trustworthy, intelligent and broad-minded independent effort, should not our universities provide investigations in the field of applied as well as pure chemistry? The carrying out of successful work in this field involves thorough search of the literature, preliminary tests, systematic experiments, carefully drawn conclusions and preparation of the work for publication. These are the normal proceedings in all research work.

Furthermore, it must be remembered that a majority of those being trained in university laboratories are looking forward to entering various industries. This is to be expected, for ours is a country in the midst of a great industrial development. We have passed through the pioneer days when the conquering of a new land, the struggle for habilitation, was supreme; so, too, has the fight for liberty of thought and action been won; and just a half century ago, in that bitter fratricidal strife, was established once and for all the fact that this is a united country. With the recovery from the wastage of that war industrial development came into its own. Manufactures are no longer characteristic of any one section, but, as labor becomes trained, are spreading rapidly over the whole land. Capital is constantly increasing and seeking profitable channels of investment.

It is important to us that the manufacturer is rapidly becoming convinced that the work of the chemist results in the substitution in industries of scientific foundation for gross empiricism, of accurate knowledge for approximate guesswork, and of lines of attempted advance based upon the results of research for the hit-or-miss method. This conviction was greatly strengthened by the address of President Little before this Society in 1913, on the subject of "Industrial Research in America."

Another call for the chemist in industry has arisen from the propaganda for conservation of our natural resources. President Bogert, in his 1908 address, pointed out clearly the important role the chemist must play in this great undertaking.

In view of the consequent increasing demand for chemists and of the relatively small number of highly trained men from our laboratories, is it small wonder that so many of our university students are looking forward to entering industrial chemistry as a profession?

In advocating a more general pursuance of research in applied chemistry in university laboratories, I do not feel that the prerogatives of the commercial industrial research laboratories of the country would be encroached upon. The field is so large and the problems awaiting solution are so manifold that the entire chemical strength of the country is insufficient to give these problems that consideration which would bring our industries promptly to the state of efficiency which can be reached only by the aid of the chemist. In the conservation and better utilization of natural resources lie sufficient problems to furnish subjects for theses in all our university laboratories.

The term "university research," however, has a broader meaning than the selection of a topic for a thesis and the systematic experimentation connected therewith. In its widest significance it is the embodiment of the university spirit itself. It typifies the relation of each university to its environment. Surely no institution can afford to be unheedful of that obligation. In its entirety it summarizes university attitude toward the complete life of the nation.

We would do well, therefore, to give serious consideration to the question often asked during the past year in a comparative way, "Is there adequate coöperation between our universities and our industries?"

I do not feel competent to attempt to answer that question categorically. Certain it is that coöperation implies the acts of at least two parties, and the question therefore directs itself with equal force to universities and to industries. Equally sure is the conviction that such coöperation would inure to the benefit of each.

For five years I was closely associated with successful business men. From that broadening experience I brought back to university surroundings no clearer impression of those men, both individually and in common council, than their desire to know the truth concerning any proposition before them, for with such knowledge they could wisely plan for the future. Desire for publication of that truth may not be so pronounced with them as with us of the universities, but the unflinching attitude towards facts, as revealing truth, is common to both classes and therein lies a strong bond of sympathy and basis of coöperation.

If that coöperation is not complete, how can the situation be improved? May I be permitted here to make a few suggestions, or rather, let me ask a few questions?

Speaking to the men of the universities I would ask:

First, of each individual head of a university chemical laboratory: What is your personal conception of the relation of your laboratory to industrial life? Do you feel that the problems in this field are fully worthy of your time and tireless thought? Do you find inspiration in the hope that your work may result directly in the transformation of some crude or now worthless natural product into a form of higher value to all, or that waste in some of its many forms shall be diminished, or that forces now acting disjointly may be so correlated that new blessings for mankind may result?

If such questions find ready affirmative, the spirit of coöperation is abroad and must make itself felt.

Second: Do we have the men of the industries often enough before our university classes?

I do not mean for the purpose of delivering formal lectures, knowing full well their aversion to the preparation and delivery of such; but surely each of these men has in his every-day life abundant experience and difficulties, the presentation of which would give sounder conceptions, broader understanding, and more intelligent grasp of conditions to be met in the work-a-day world ahead.

Third: Are we sure that we give our lectures on industrial chemistry, especially to undergraduates, from the best point of view?

A recent experience may be worth recording here. For several years I followed the lines usually adopted in standard texts, but the division into inorganic and organic technology seemed artificial, in view of the preachments on that subject during the previous course in general chemistry; the usual grouping of topics seemed to be very loosely connected; in fact, the course lacked unity of purpose and sound pedagogical basis. I finally determined to change the whole point of view, and gave a series of lectures on "Staple crops and natural resources as affected by industrial chemis-

try." For illustration, and without going into detail, the cotton crop was discussed: its demands on the fertilizer industry, following the fiber through its changes by bleaching, mercerization, mordanting, dyeing, printing, nitration, etc.; then following the seed through the mill and the conversion of the hulls into feed and paper, the use of the meal as feedstuff, the refining of the oil, its hydrogenation, the utilization in the soap industry of the waste in refining, the recovery of the glycerine and its nitration. In this way all the subjects treated in former years are covered, but in an entirely different order. The predominating thought is chemistry in the service of mankind. New conceptions are obtained of material blessings, of inter-relations of industries, of utilization of by-products, of advances already made and of promising lines of further advance. At the end of the year there is a complete picture in the student's mind, an awakened interest in his material surroundings, a true comprehension of the part chemistry has played in this industrial development, and, in many cases, a determination formed to join the ranks of chemists in carrying forward this development. The results already obtained from such a treatment of industrial chemistry abundantly justify the change.

Speaking to the men of the industries I would ask:

First: Is not your interest in our universities very remote, if indeed it exists at all?

Yet in them are being trained young men whom, in constantly increasing numbers, you will call to your aid to promote the efficiency of your operations and thus enable you to meet the keener competition of the future; in their libraries is a technical literature which will put you in immediate touch with the latest developments in fields of direct interest and importance to you; and on their staffs of instruction are men trained to think accurately, to investigate skillfully, and with whom frank discussion of manufacturing difficulties would often lead to valued connections.

Second: Is a visit to your plant by an instructor and his group of students simply a thing to be endured or gotten through with as rapidly as possible by the aid of some subaltern who lacks your knowledge of the larger aspects of the industry in which you are engaged?

Such occasions could be made of inestimable value in cultivating true cooperation between industries and universities.

Third: Would it not be possible to include university men more frequently on the programs of industrial conventions?

Such a policy would be a mutual help, stimulating thought and breeding good-will.

Fourth: Have you aided our universities in a material way?

Coöperation is mutual helpfulness. Many of the fundamental principles of present-day industries have been worked out in university laboratories. You can aid in many ways; by furnishing material prepared under factory conditions for use in research in university laboratories, by contributing equipment which will widen the possibilities of such work, by enlarging department libraries which constitute the prime prerequisite of all research laboratories, and by endowing fellowships which will enable many a promising young man, otherwise unable, to continue his work through that unremunerative period of higher training which is requisite if he is to realize his highest possibilities.

I know of no more fitting illustration of the spirit of coöperation in matters chemical than the organization and wise general policies of this Society. In its large and constantly growing membership are included the university men and those directly connected with the industries. By joint effort and with increasing enthusiasm an organization has been developed which is daily increasing in value as a national asset.

Its general meetings, stimulating interest in chemistry in whatsoever section of the country held, are participated in by both classes of chemists, and the healthy, broadening influence of this contact is appreciated by each alike.

Its three splendid journals are placed in the hands of every member. While the subject matter of these journals is differentiated, it is rightly assumed that each is of importance to every member and the three as a whole thus furnish the greatest of all influences in the development of chemistry in our country.

Rapid growth in membership and increased productivity in research rendering impossible the completion of programs at general meetings, divisions were organized under the administration of President Bogert. Reasonable opportunity is thus afforded for such specialization as may be desired, but membership in these divisions is open to all and attendance is composite.

Occasionally a note is heard that we should divide into two separate organizations, the university men in one and those of the industries in another. Happily that note finds no response of any general character and I sincerely hope it never will.

For the sake of the future let me point out one of the best features of our organization, and yet one which holds within itself the gravest danger if the spirit of coöperation be not all-pervasive. I refer to our Local Sections. With a membership distributed over such a wide area and with only two general meetings of the Society held each year, such local sections furnish to many almost the sole opportunity for fraternal

association, for discussion of matters of somewhat restricted interest, for bearing the expense of invited lecturers and for placing before the Council the views of the respective sections on matters of general policy of the Society. These are some of the strong points of this feature. The danger lies in local-sectionalism, which magnifies the part at the expense of the whole, which in the effort to advance locally is forgetful of the common good. The danger is insidious and often clothes itself in the guise of the broader sentiment, but it is all the more grave for this reason. Let us hold fast to all the elements of strength in our local section system and see to it that only good flows therefrom to the parent organization.

Another and novel form of coöperation in matters chemical has recently manifested itself in the form of an invitation from the Secretary of the Navy to our Society to nominate two of its members to serve, with representatives of other scientific societies, on the proposed Naval Advisory Board. I am sure you will approve my prompt acceptance, in your behalf, of this invitation. To secure the nominations promptly and in the spirit in which the invitation was given, the Council was asked to make these nominations as it is closely in touch with the full membership of the Society through the local sections. The result of the letter-ballot has been communicated to the Secretary of the Navy and will be announced by him.

That the spirit of coöperation is beginning to make itself felt is evidenced by the joint participation of the chemical manufacturers in this country and of the government bureaus in the first National Exposition of Chemical Industries to be held this month in New York City. This assemblage has in it great potentialities which, if realized, may have far-reaching influence in the rapid promotion of hitherto undeveloped lines of chemical industry.

In conclusion, let me discuss with you one other phase of coöperation, namely, that between the American people, through their representatives in Congress, and our chemical industries. I have no leanings toward paternalism, and I believe in the doctrine that a good, stiff struggle for existence is conducive to longevity, but there are certain normal functions of our national Congress which make or mar industrial development, and there are certain undertakings in behalf of the nation as a whole which individuals can not be asked nor expected to assume.

Recent events compel the conviction that the assumption of our peaceful world relations, which formed the basis of my earlier plea, may be at any moment completely shattered. In such an event the responsibility of all chemists in this country will be added to by the impelling

call of patriotism. That the contributions of our science are of the highest value in modern warfare is daily attested in the reportorial accounts of the new developments among the now contending nations. Who would dare say that the innovations of chemistry in the methods of warfare have reached a limit?

In view of this recognized fundamental importance would it not be well, in these days of talk of preparedness, to consider the question of chemical preparedness. Ships, guns and shells are necessary, yes, but most largely as a means to an end, and that end the effecting of a violent chemical reaction at a point more or less distant. Naturally in matters of preparedness there are topics whose public discussion is inadvisable, but there is one to which I do not hesitate to allude, for the facts are all matters of published record, and that is the question of the visible supply of sodium nitrate in this country.

In these days of rapidly shifting international relations the only sound and rational policy is national self-containedness. Blessed with a rich heritage of wonderful and varied natural resources, and, in our isolation, confident of freedom from grave international complications, we have received potash supplies from Germany with but scant forethought, save in the national Bureau of Soils; and now, today, agriculture is seriously threatened; so too textile manufacturers, reaping a bountiful harvest from the laboratories and dyestuff factories of Germany, have given no helping hand to the struggling young home industry which with a fair show would now have been able to meet the present serious deficiencies. Of far greater importance, at least from the standpoint of preparedness for war, is the fact that at present we are dependent solely on Chili for supplies of sodium nitrate, the crude material for nitric acid, that *mine qua non* in the manufacture of all modern explosives, whether guncotton, trinitrotoluene, picric acid, fulminating mercury or what not.

True, the work of the chemist has shown in later years how to prepare this substance from the nitrogen of the air, but such processes have not been able to compete commercially in this country with its manufacture from sodium nitrate and sulfuric acid. Equally true, we now see no immediate probability of any shutting off of the supply of nitrate from Chili; in the question of preparedness for war, however, probability has no place where certainty can be assured.

It would seem the part of wisdom, therefore, to accumulate, through governmental aid or agency, sufficient extra supplies of sodium nitrate to assure, in case of war, maximum activity of explosive manufactories until sufficient plants could be erected for the adequate manufacture of nitric acid from the air. The annual importation of this material

averages 550,000 tons, which represents an investment of approximately fifteen million dollars. The presence of an extra year's supply within our borders might prove of inestimable value. If, happily, the war cloud passes, such accumulations of nitrate would then be gradually absorbed in the more peaceful lines of the fertilizer industry, and the cost of such preparedness be thus limited to the expense of storage and the interest on the funds invested.

The phrase "chemical preparedness" refers really to the whole question of the status of chemical industry. Have we so grappled with the many questions of material national life that we can await future political developments with quiet confidence and utmost faith? Undoubtedly much has been accomplished, but this is no time for self-congratulation. Far more profitable will it be to look shortcomings squarely in the face, to trace influences which have retarded progress and to endeavor in every legitimate way to overcome such influences. Time does not admit of too extensive treatment of this subject, but there are two matters whose present importance justify further discussion. I refer to the patent system and to our tariff legislation.

The apparently authentic statement that more money is spent in this country to secure and defend patents than is earned from all those issued seems a sad commentary either on the morals of the nation or on the efficiency of the patent system. With a natural unwillingness to admit the first alternative we are forced then to ask wherein lies the deficiency of the patent system?

Primarily, and of greatest importance, is the failure of our people as a whole to understand the purpose of a patent system and its value as a national asset. Its purpose is to foster a creative spirit throughout our citizenry by giving to intellectual rights that legal protection in ownership which is afforded property rights, such ownership carrying with it the right to profit therefrom. He who creates is entitled to remuneration, for by his originality he places the nation in his debt. Such indebtedness is no hardship, for the patentee takes nothing away, but makes his entry in advance on the credit side of the national ledger. That such entries may represent maximum creative ability, it is essential that they be made in an atmosphere of good-will and in full confidence of due and prompt guardianship of the account.

Too often the attitude of the public is one of antagonism to the patentee, and too often manufacturers, pursuing a short-sighted policy, endeavor in every way to evade his legally conferred rights. Is it a worthy thought on the part of "business," that, since inventive genius so often lacks business qualifications, it offers a fair field for commercial piracy? Let us shake off such thoughts and by coöperation seek to promote that

creative spirit, the fostering of which lay in the minds of those who founded the patent system.

The value of the patent system as a national asset lies not only in the constant additions to daily welfare, but also in the eventual public ownership of the new ideas underlying these contributions, for the life of a patent is only seventeen years, during which time expenditure both of brain and of funds is necessary to bring the idea to its highest practical development; then the idea legally becomes the property of the nation for unrestrained use. Are we willing that this national asset should be depreciated by an unending tax on the time, thought and finances of composite American genius?

If these general considerations ever find full lodgment in the public mind, there will be no difficulty in securing such congressional action as will perfect the patent system and legal procedures incident thereto, thus enabling it to serve fully those high ends for which it was designed.

Finally, in the light of the present situation, may we not hope for more generous coöperation between Congress and our chemical industries in solving those innate economic difficulties whose temporary correction can be provided for only through adequate tariff legislation? I realize fully that the trend of national opinion in recent years has been toward a lowering of tariffs, in the conviction that industrial giants were parading in the guise of swaddling clothes, but the present unforeseeable situation, resulting in the cessation of imports from the chemical industries of Germany, has shown to all several strikingly weak links in our industrial chain. We can not afford such. "National self-containedness" is a more fitting slogan for us now than "Tariff for revenue only." If such links are to be strengthened, we must, as a people, meet the expense by giving for a reasonable time that measure of protection which will effect a union of capital and scientific skill under no undue stress of unfair foreign interference.

No other phase of our chemical industry illustrates so well the point in mind as the synthetic dyestuff industry about which so much discussion has turned during the past year and concerning which even more active discussion is destined to be furnished during the year just ahead of us. Although the clamor over the shortage of synthetic dyestuffs in the early period of the present war was shown by undeniable statistics to have had no basis in fact, nevertheless the present complete cessation of shipments from Germany and the constant inroads on the stocks in hand have now brought about a real and serious shortage.

True, the total annual value of our needs in this line, some fourteen or fifteen million dollars, including duties paid, is not large as compared

with the volume of many other industries, yet the use of the products is so ramified throughout industrial life, reaching in some way so many manufacturing plants and threatening to affect so many laborers that the question naturally finds anxious utterance—"What can we do about this shortage?" This question can be answered best by an unflinching facing of what we as a people have done, and, equally important, what we have not done.

The synthetic dyestuff industry stands today as Germany's triumph. It has been developed partly by that hearty coöperation of industries and universities to which I have already referred, and partly by favorable legislation. It is permeated in every branch by the spirit of research. In its interlacing character it is bound together by reasonable, common-sense coöperation, and it is long past the experimental stage with these attendant heavy financial losses.

At one time we had a young industry, nine factories in all. It is interesting to note that during the decade 1872-1882, with a tariff of 50 cents per pound and 35 per cent. *ad valorem* then in force, the price of "aniline red," the principal dye then in use, was reduced from \$6.50 to \$2.25 per pound. With the lowering of the tariff on dyestuffs in 1883, five of the factories ceased operations. I am not arguing the wisdom of such legislation, but am simply stating facts. Further, it is a matter of public record that the most earnest advocates of tariff reduction on dyestuffs and opponents of its increase were those who are now rightly so alarmed about the present shortage. Again I do not criticize, but state facts in explanation.

In spite of these difficulties one of our factories successfully undertook at one time a considerable production of aniline oil and other intermediate products for which we had depended, up to that time, on foreign countries. What was the result? A market flooded with these products from abroad at prices far below American cost of production. Why? For the express purpose of throttling the new effort in this country, the quintessence of "dumping."

What could be done in such a situation? What can be done today in any similar situation? It is a task too great for economic enterprise and there is no legal redress. In our intra-national conduct of business we have, by effective national legislation, put the stamp of public condemnation on this practice of dumping, and have insisted that in business relations with each other the spirit of true democracy must reign, granting to each full opportunity to develop to that maximum to which talents and energy enable and entitle. I badly misjudge the temper of our people and their spirit of fair play, which is the essence of democracy, if, given opportunity to understand this situation, they do not speedily set

about to correct, through their representatives in Congress, this serious defect in national legislation by the enactment of an effective "anti-dumping" clause.

To meet the present deficiency in dyestuffs some progress has been made. Naturally the use of vegetable dyes, at one time our sole dependence, has materially increased. One synthetic dyestuff factory has felt justified, through the agency of long term contracts at trebled prices with its customers, in undertaking the manufacture of those "intermediates" necessary in the manufacture of its specialty. The extremely high prices at present ruling have stimulated the organization of a few more manufacturing concerns. The Department of Commerce is seeking to aid in many ways. The outlook for raw material has improved through the realization of its waste in the beehive coke ovens, though most of the increased recovery is at present finding its way into the manufacture of explosives. After all is said, however, the serious deficiency still exists and will continue unless the day of peace be inconceivably near, or prompt and effective measures be taken.

It may seem strange that, with an intense demand for its products, an assured supply of raw material, and an abundant supply of technically trained chemists, the American dyestuff industry shows as yet no evidence of that full expansion which will enable it to meet the present crisis and provide in the future for our constantly growing needs. The explanation is simple: capital is not convinced that investment in such an industry, under present conditions, is profitable or safe—and rightly not convinced, because the opinions of experts, familiar with every phase of this industry in Germany and in America, agree that under present tariffs it would be unprofitable, and past experience with German practice justifies the fear of inordinate dumping, which will take place in the inevitable struggle to regain markets, following the return of peace.

The prime consideration, therefore, in the immediate development of this industry in our midst, is congressional action in the form of an effective anti-dumping clause and an increase, for a reasonable period, of the present tariff on dyestuffs. As a guide to what this increase should be, we have the judgment of the committee, of the New York Section of this Society, a committee representative of all interests concerned, in the persons of: B. C. Hesse, chemical expert in coal-tar dyes, *Chairman*; H. A. Metz, for the importers; J. B. F. Herreshoff, for the manufacturers of heavy chemicals; I. F. Stone, for the American coal-tar dye producers; J. Merritt Matthews, for the textile interests; David W. Jayne, for the producers of crude coal-tar products; and Allen Rogers, Chairman of the New York Section. The unanimous report of this committee, which was unanimously adopted by the Section, says: "It has been conclusively

demonstrated during the past thirty years that the present tariff rate of 30 per cent. on dyestuffs is not sufficient to induce the domestic dyestuff industry to expand at a rate comparable with the consumption of dyestuffs in this country and that, therefore, all dyestuffs made from coal tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal tar, should all be assessed alike, namely, 30 per cent. *ad valorem* plus $7\frac{1}{2}$ cents per pound specific, and that all manufactured products of or obtainable from coal tar, themselves not dyes or colors and not medicinal, should be taxed 15 per cent. *ad valorem* and $3\frac{1}{2}$ cents per pound specific."

Are the people of this country ready to coöperate with the chemist by authorizing the prompt enactment of such legislation? If so, there need be no fear that active capital will be longer withheld, and thus we can feel confident of a synthetic dyestuff industry commensurate with our needs.

As I think of the possibility of such an industry, I recall the words of the Swiss professor, Gnehm, who, in 1900, after one of his lectures on coal-tar dyes, said to me: "The natural home of the dyestuff industry is in your country and some day it will flourish there."

The creation of such a self-contained industry, however, has far deeper meaning for our national welfare than the supplying of needed dyestuffs for such plants would constitute an easily convertible reserve for the manufacture of coal-tar explosives in times of war.

Through its stimulative effect on research, on technique and in supply of material the dyestuff industry has furthered the development of both the explosives and the medicinal industries. Its firm establishment here would foretell the complete development of each of this great trio of industries, which, as a whole, furnish the rational and economic utilization of that great mass of coal tar which now wastes itself in useless flames above the coke ovens throughout the land.

Coöperation—it is a good word, and carries with it a wonderful power of accomplishment!

CHAPMAN HILL, N. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]
**THE REDUCING POWER OF PHOTOGRAPHIC DEVELOPERS
 AS MEASURED BY THEIR SINGLE POTENTIALS.**

BY FRANCIS C. FRARY AND ADOLPH H. NIETZ.

Received July 28, 1915.

One of the most important properties of a developer is its reducing power, as measured by the free energy of the reaction when it is on

dized. It is evident that this must be adjusted to lie within certain limits; to insure proper development of the image on the one hand, and on the other to avoid the production of chemical fog, due to the development of unexposed silver bromide. No direct determinations of this property have hitherto been made. Sheppard and Mees,¹ by an indirect method depending on the restraining power of potassium bromide, have obtained values representing the relative reducing power of *p*-aminophenol, hydroquinon, hydroxylamine and ferrous oxalate developers. Assigning a value of 1.00 to ferrous oxalate, they find the following numbers for the other developers: *p*-Aminophenol, 3.4; hydroquinon, 0.6; hydroxylamine, 1.13.

Mathews and Barmeier,² and Lidbury,³ have recently published some work on the single potentials of various developers, but have neither given data nor suggested a method by which either absolute or relative reducing powers of these developers could be determined. It is to be noted that the observations of Mathews and Barmeier extended over periods of only six to twenty hours, in which time it is impossible to even approach equilibrium values for the single potentials. Lidbury extended his observations over a longer period of time, but frankly states that he did not consider that he obtained equilibrium values. The determinations of Mathews and Barmeier are also obscured by an error in calculation, apparently due to a false conception of the sign and use of the normal calomel electrode. They drew certain conclusions from the shape of the curves representing the value of the single potential as a function of the time; but, as will be shown later, the shape of these curves is incidental to the approach of the equilibrium, and in no way a basis for the conclusions which they draw.

In this work we shall attempt to show:

(1) That the more or less rapid variation of potential observed during the first period (sometimes for weeks), shows absolutely nothing concerning the real single potential of the developer, no matter what form the curve may take. Nearly all developers start at about the same point and closely parallel each other for some time. At any rate, these initial changes are unimportant and incidental; it is the final point of equilibrium alone which can give us the desired information. The attainment of this presents many difficulties, as later experience shows.

(2) That it is impossible to consider a fall of potential as being due to oxidation of any sort, much less that of the sulfite, as suggested by Mathews

¹ Sheppard and Mees, "Investigations of the Theory of the Photographic Process," pp. 188-196 (Longmans, Green & Co.).

² Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, 20, 201.

³ Lidbury, *Ibid.*, 20, 189, 193, 197.

and Barmeier. Moreover, these changes can not be due in any degree to the sulfite present; it is probable that the sulfite plays a minor role in the mechanism of the developer.¹ But it seems to be established by experience and experimental evidence that the carbonate is a very important factor. Our reasons for not agreeing with the sulfite-oxidation theory of the cause for falling potentials are presented in the following pages, which give a theory that has been based entirely on experimental facts.

In addition, the fundamental theory of the production of a difference of potential between the electrode and the developer and the conditions preventing the immediate attainment of its true value will be discussed. The explanation of curves such as those obtained by Mathews and Barmeier will be obvious. A method of determining both the absolute and relative reducing power of a developer will be discussed and employed.

Theoretical.

The cause of a difference of potential between a platinized platinum electrode and a developer must be the gaseous hydrogen formed in the developer and deposited on the electrode. The electrode potential will then be a function of the partial pressure of the hydrogen on the electrode and the hydrogen-ion concentration of the developer. The production of hydrogen probably takes place in the manner indicated in the following ionic reaction:



where R represents the active portion of the reducing agent in the developer, and no assumptions are made as to the way in which it combines with the oxygen. It is evident that the concentration (and therefore the partial pressure on the electrode) of the hydrogen produced depends on the temperature, the concentration of the reducing agent, and the nature of the latter. Since the product of the hydroxyl-ion and hydrogen ion concentrations is constant at any given temperature, the only way in which the alkalinity of a developer can affect its reducing power is by changing the concentration or nature of the active portion of the reducing agent. It is probable that the reducing agent is present in the form of sodium salt, more or less hydrolyzed and dissociated, and that the active portion consists of the anion formed in the dissociation. It is probable that the greater part of the effect of the carbonate in conditioning the velocity and density attained in development is due to its action in swelling the gelatin and thus facilitating the action of the developer on the silver salt.

Since the single potential of a developer depends both on the alkalinity

¹ Sheppard and Mees, *Loc. cit.*, p. 179.

of the solution and the concentration or pressure of the hydrogen on the electrode, and the latter alone is the measure of the reducing power of the developer, it is obvious that a direct comparison of the single potentials of developers would give us no information as to their relative reducing powers. Nernst¹ states that the reducing power is greater according as the gas evolution (hydrogen) takes place at a higher pressure. In order to determine the absolute pressure of hydrogen represented by a given single potential E_s of a developer, it is only necessary to also determine, in the same solution, the potential E_{H_2} of a platinized electrode saturated with hydrogen at atmospheric pressure. For two hydrogen electrodes in the same solution, but saturated with hydrogen at different pressures, the difference of potential is represented by the formula

$$E = 0.0001983 T \log C/C',$$

where C and C' represent the hydrogen pressures. Since the pressure in one case is known to be one atmosphere, $C = 1$, and at 25° the equation becomes

$$E = 0.05909 \log 1/C',$$

E being the difference between the hydrogen potential of the developer and its single potential ($E = E_{H_2} - E_s$). This partial pressure of hydrogen (C') seems to be the only absolute standard to which the reducing power of the developer can be referred.

By determining the hydrogen potential (E_{H_2}) of the same developer in several stages of oxidation, it was shown that, in the case of hydrochinon at least, the alkalinity of a developer was not affected by its oxidation, and no error is therefore introduced by any such change during the determination.

In such a complex system it should not be expected that equilibrium would be at once obtained. When it is finally reached, it is obvious that the electrode, the solution, and any space above the solution, must all be saturated with hydrogen at the same partial pressure. The attainment of this condition is delayed by two different types of causes: chemical and physical.

Of the chemical causes, the presence of oxygen in the solution is at first very important. This continually dissolves in the platinum and acts as a depolarizer, until it is all consumed. The extent of this delay is determined by the quantity of the oxygen and by the difficulty with which the last traces of it may reach the electrode. Another chemical cause, which seems to be particularly important in the case of hydrochinon, is a sort of reaction-resistance, apparently inherent in the substance itself, and probably allied with the initially low chemical velocity found

¹ Nernst, "Theoretische Chemie," 5th ed., p. 740.

in the hydrochinon developer by Sheppard and Mees.¹ We were able to eliminate the errors due to the presence of oxygen by making up the developer *in vacuo* with special precautions, and by this means obtained equilibrium within a week for amidol, but were unable to approach it with pure hydrochinon developers in three months. A hydrochinon developer made up with 0.5 g. tetrathiourea ammonium bromide per liter, seemed to come to an equilibrium very quickly at a potential indicating much higher hydrogen pressure than would be expected for hydrochinon. After maintaining this potential for a week, the very small quantity of the thiourea salt seemed to have been decomposed by the alkali, and the potential very quickly rose to approximately the value previously obtained for metol-hydrochinon, and probably nearly correct for hydrochinon alone. This value was maintained for six weeks. Apparently the thiourea salt either lowered the reaction resistance or aided in bringing about a condition which the hydrochinon was able to maintain after the thiourea salt was decomposed.

The physical causes all concern the problem of getting the hydrogen to the electrode, and the mechanical removal of the hydrogen. In order to study these it will first be necessary to consider the manner in which the hydrogen gas is produced. Either it is produced by the developer through the catalytic action of the platinum black, and therefore directly on the electrode, or it is formed throughout the solution and is extracted by the platinum electrode on account of its solubility in platinum black. Bubbling an inert gas through the solution at the electrode causes an immediate rise in the potential, which might be due to the mechanical removal of the hydrogen from the electrode by the gas. If the hydrogen were formed at the electrode only, on account of the catalytic action of the latter, stirring the solution in a closed cell completely filled with liquid should have the same effect, to a smaller extent, as bubbling an inert gas through the solution. The fresh solution should dissolve hydrogen out of the electrode and cause its potential to rise (become more positive). As a matter of fact, many experiments along this line, which they have given any results at all, have produced a lowering of the potential, caused evidently by an increase of hydrogen concentration on the electrode. It would appear most probable then, that the hydrogen produced throughout the solution and extracted by the platinum black. The attainment of equilibrium between the platinum and the solution is therefore physically hindered by the slow diffusion of the hydrogen through the developer toward the platinum, and from the liquid into the metal itself. Similarly, the hydrogen must diffuse through the liquid and from the liquid into the space above, before the partial pressure of the

¹ Sheppard and Mees, *Loc. cit.*, p. 169.

gas in that space can correspond to that of the hydrogen in the solution.

Since an increase of the concentration of the hydrogen on the electrode makes it more negative with respect to the solution, the potential will continue to change in this direction until the hydrogen gas is in equilibrium with the solution, the platinum of the electrode, and the space above the liquid surface. These considerations alone are evidently sufficient to explain the fact that the single potential of a developer changes very rapidly at first and then more and more slowly, giving curves of the shape shown by Mathews and Barmeier. Therefore the shape of these curves can not be cited in support of their views as to the function of the different constituents of a developer.

Experimental.

All single potentials were measured with the aid of a large potentiometer (Kompensations-Apparat nach Franke¹) and a very sensitive galvanometer. The potentiometer was frequently adjusted by the use of a Weston cell, which had been made up for more than a year and was compared during the preliminary experiments with a cell certified by the Reichsanstalt. The normal calomel electrode was used, being assigned the value $0.560 + 0.0006(t - 18)$, the mercury being considered positive to the solution.² All single potentials are given as the potentials of the electrode minus that of the solution ($E_{Pt} - E_{sol}$). The error in the determinations of the potentials is of the order of 0.001 volt or less, usually no more. A saturated solution of potassium chloride was used as the intermediate liquid in all cases.

The first experiments were made with an electrode cell consisting of a 250 cc. bottle, partially filled with developer, and closed with a rubber stopper, through which passed the necessary glass tubes. The solution was a metol-hydrochinon developer recommended for use with Seed plates, having the composition, in grams per 1000 cc. water: metol 1.85 g., hydrochinon 1.85 g., sodium sulfite 13.9 g., sodium carbonate 13.9 g. The carbonate used in this formula was Merck's C. P. dried, which was later found to contain 14.8% water. The sulfite was Baker's analyzed anhydrous, which was that used throughout all our experiments.

The curves, of which Nos. 1 and 2, Fig. 1, are examples, have the slope required by the theory. After several hours the curve begins to rise again (not included in the figure) and the developer becomes yellow, evidently on account of oxidation. The oxygen absorbed has, by its depolarizing effect, distorted the curve, prevented the attainment of equilibrium, and has oxidized the developer so that it is finally unable to

¹ *Z. Instrumentenkunde*, 23, 93 (1903).

² Ostwald Luther, "Physiko-Chemische Messungen," 3rd ed., p. 443.

produce hydrogen as fast as the latter is oxidized at the electrode, and the potential begins to rise again. Mathews and Barmeier have stated that the existence of the first part of the curve, where the electrode is becoming more and more negative with respect to the solution, is due to

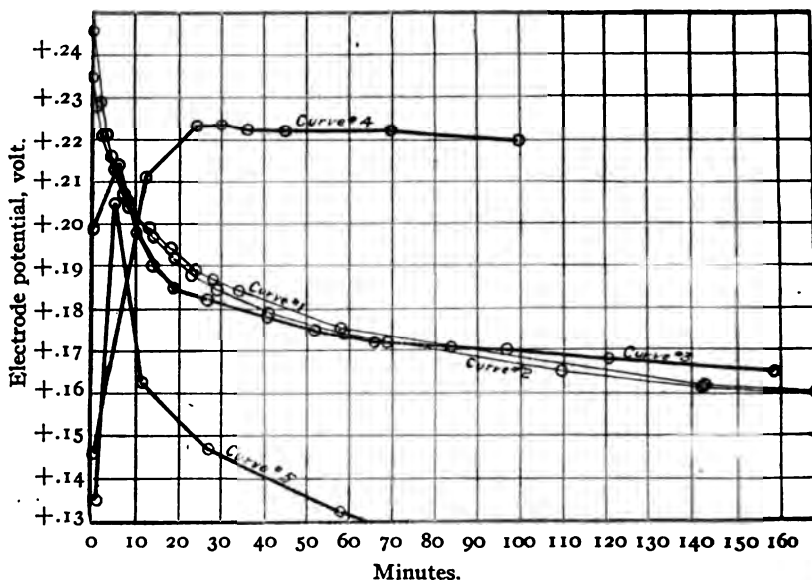


Fig. 1.—Electrode potentials in developers.

the oxidation of the developer, but it is evident that the *later* portion of the curve, where the potential is becoming more and more positive, is really the one where the effect of oxidation appears.

To show the effects of oxidation and mechanical agitation, two cells were used which had been set up for some time, and had already attained fairly low values for the electrode potentials. Air was bubbled through one of these, and nitrogen through the other. The results are shown in Curves 3 and 4, Fig. 1. The values plotted at zero time are those taken just before the gas was turned on. In both cases it will be noted that there is an immediate rise in the potential of the electrode, evidently due to the removal of hydrogen from the platinum. Curve 3 shows that when nitrogen is used, and the effect is purely mechanical, this rise is succeeded by a drop, after which the curve tends to become horizontal. The rise at first is apparently due to the agitation, which brings to the electrode a surface layer of developer richer in oxygen. This at once reacts with the hydrogen in the electrode, but the passage of the nitrogen both tends to remove oxygen already in the developer and to prevent more from entering it. The potential then drops rather rapidly as the

electrode absorbs hydrogen from the solution, while the nitrogen, by tending to remove this hydrogen, flattens out the curve and soon is able to remove the hydrogen as fast as it is formed. If the nitrogen is now turned off, the curve drops rather suddenly as shown in Fig. 2, since the interfering action of the nitrogen is removed.

Curve 4, Fig. 1, shows the electrode potential when air is bubbled through the solution and the depolarizing effect of the oxygen is thus maintained. The difference between Curves 3 and 4 can only be ascribed to the oxygen in the air, and refutes entirely the claims of Mathews and Barmer as to the effect of oxidation of the developer. After the two cells had run in this manner for some time, they were interchanged, the one containing nitrogen being now supplied with air, and *vice versa*. The new curves for agitation with nitrogen and air were almost identical with

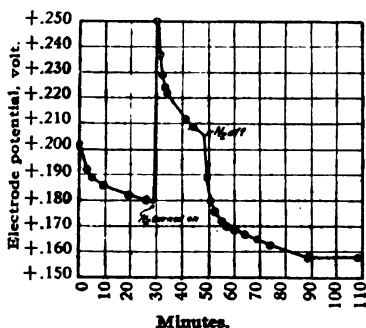


Fig. 2.—Effect of a current of nitrogen on the electrode potential in a developer.

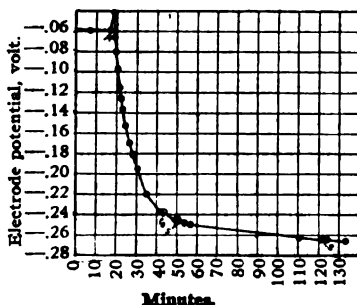


Fig. 3.—Electrode potential in developer with hydrogen passed through the solution.

Curves 3 and 4, thus indicating that the shape of these curves was determined entirely by the composition of the gas used.

A similar mechanical effect was observed when a cell was shaken vigorously for half a minute, and the potentials then read at intervals (Curve 5, Fig. 1). If the potential of a developer is taken by means of an electrode dipping into it in an open dish, and the solution is stirred, the results are the same.

A current of hydrogen was passed through a cell which had been set up for several hours and which had attained a nearly constant value of -0.060 volt. The results are shown in Fig. 3; the hydrogen being turned on at point A, 18 minutes after the beginning of the portion of the curve shown. A slight rise, due to depolarization by dissolved oxygen from the surface of the developer, is again observed, followed by a rapid drop, due to the saturation of the platinum with hydrogen. At each of the three points marked S, the cell was shaken vigorously for half a minute,

and it will be noticed that the effect, which was slight at first, becomes negligible as the electrode approaches saturation. This is exactly what would be expected from the explanation already given. This curve has the same general characteristics as the previous ones, and those of Mathews and Barneier, and substantiates the theory of the causes of the retardation of the equilibrium in the determinations of the single potential of developers.

In order to obtain the real single potential of a developer, it is evident that an apparatus, entirely constructed of glass, must be completely filled with the developer and the observations extended over a long time, until it is quite certain that equilibrium is reached. The form of electrode cell finally adopted is shown in Fig. 4. The total capacity up to the stopcock B is about 4 cc. At D is a constriction, so that, after filling, the apparatus may be evacuated and sealed off. E is a small platinized electrode. The side-tube is drawn to a fine point at C, which is plugged with filter paper after the cell is filled. A short piece of rubber tubing with a glass plug closes the end C'. At first these cells were filled as follows: the developer was quickly mixed and drawn up to point F, the stopcock was closed, the cell evacuated with a water pump and sealed off at D. After cooling, C was placed in a small amount of the developer and the stopcock opened, whereupon the cell filled almost completely, leaving only a small bubble of air over the solution. The plug of filter paper was inserted in C, and the apparatus was ready for use. With this cell the Seed metol-hydrochinon developer reached, after six weeks, a fairly

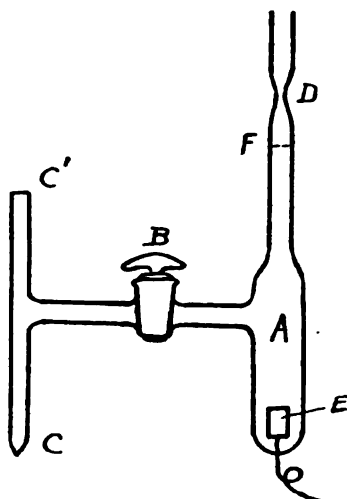


Fig. 4.—Cell for determining the single potential of a developer.

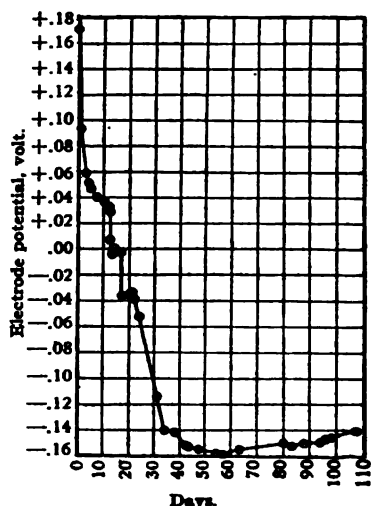


Fig. 5.—Electrode potential of Cell No. 3, Developer No. 1, Jan. 15, to May 2.

constant value of -0.150 volt. Four different cells containing this developer ultimately gave the same reading, maintaining it for a period of nearly two months. Fig. 5 shows the observations on one of these cells. Many minor irregularities are to be noted. As stated on page 2236, the carbonate used in this developer contained about 15% water. On account of the importance of this salt, it was decided that later determinations should be made with thoroughly dried material.

Suspecting from the behavior of the cells that some of the irregularities shown in Fig. 5 might be due to inhomogeneity of the solution, small rods of glass were put in some of the cells to act as stirrers. With the use of these it was at times possible, when a temporary equilibrium appeared to have been reached, to disturb this and start the potential downward. No uniformity could be traced in the results of shaking, although it was observed that there was a certain stage, between $+0.035$ and -0.040 volt, where the cell was more sensitive to shaking. Some of the cells reached a temporary equilibrium which might have proved very misleading, if only one determination were made. One of the cells containing this developer remained at $+0.035$ volt for more than ten days, another at about zero for several days, and a third seemed constant at about -0.036 for a week.

With the hope of hastening the attainment of the equilibrium and further eliminating sources of error, an apparatus was designed and made whereby the developer could be mixed *in vacuo* with oxygen-free water, and then filled into electrode cells of the same design as shown in Fig. 4, the latter having also been evacuated and washed out with both nitrogen and the developer. The apparatus and its use will be described together. The apparatus is shown in Fig. 6.

The tube V is connected with the vacuum pump, N with the nitrogen supply (made from ammonium nitrite and washed with alkaline pyrogallate in a Liebig potash bulb), and the tube M is connected with the tube C of the cell. All the glass parts have been previously cleaned with chromic acid and washed with distilled water. The tight rubber stopper S is put in place, and the tube now evacuated. H is a stopcock so arranged that the suction can be applied either at J or C. A tight rubber tube and glass plug are placed over C'. For the first part of the operation the suction is applied at J, the stopcock R being open while B is closed. When most of the air has been removed from the mixing apparatus and the cell, nitrogen is slowly admitted at C, and J is closed. The apparatus is allowed to fill with nitrogen, is then evacuated as before and again filled with nitrogen. Tube T is large enough to contain about 75 cc., and should be about 20 cm. long. It is graduated for 25 and 50 cc.

About 100 cc. of distilled water are boiled for ten minutes in air. The stopper S is loosened and the stopcocks so arranged that a rather brisk stream of nitrogen will flow through the apparatus from C when S is removed. The stopper S is now removed and about 35 cc. of the boiled water quickly introduced into the apparatus by means of a pipet. The

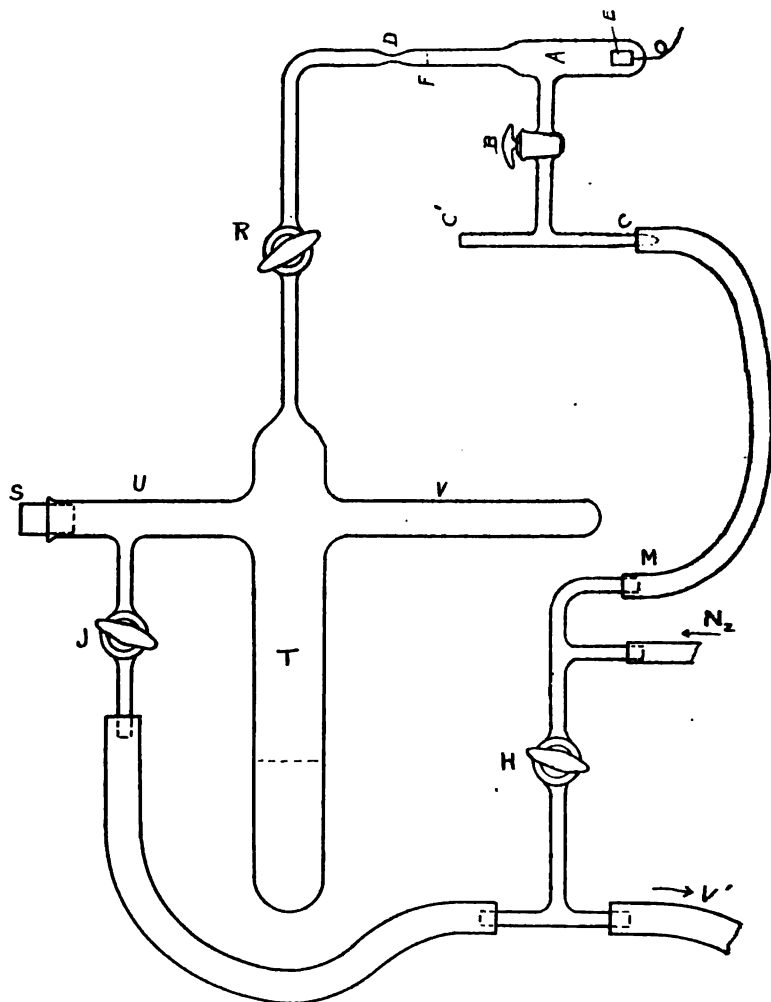


Fig. 6.—Apparatus for making up developer and filling electrode cell *in vacuo*.

stopper is then again inserted, the nitrogen supply shut off, and suction again applied slowly at J, until the water boils vigorously. A slow stream of nitrogen is now allowed to flow through the apparatus from C, and the boiling *in vacuo* cautiously continued, with gentle heating. After

boiling ten minutes, the suction is shut off and the apparatus allowed to fill with nitrogen and cooled. The volume of the water should be adjusted to 25 cc. by drawing out the excess through J. The developer, previously accurately weighed into small glass capsules, is now introduced through the tube U, while a current of nitrogen flows through the apparatus as before. The capsules are dropped into the tube V by inclining the apparatus, or carefully placed in the tube U, but are not allowed to come in contact with the water. The stopper S is now put in tightly, and the apparatus evacuated as far as stopcock B. It is then filled with nitrogen, again evacuated, and again filled with nitrogen. The capsules of developer are then dropped into the water and quickly shaken until the contents are dissolved. Suction is again applied, and the nitrogen dissolved in the water during the solution of the developer is mostly removed. Nitrogen is once more admitted, and the whole apparatus evacuated. By tipping the apparatus, about 3 cc. of developer are allowed to flow into the electrode cell A. R is now closed and the developer shaken around in A to rinse it out. Suction is now applied at C, drawing out the air up to the stopcock B. A little nitrogen is admitted at J, and R is opened. On now opening B, the developer in A is drawn out and the cell rinsed. B is then closed, and another portion of 3 cc. allowed to flow over and drawn out by way of C as before. The greatest possible degree of suction is now applied at C, and B is closed. The cell is now filled to a point about 2 cm. beyond the stopcock B, leaving a space of about a centimeter above the developer in the cell, so that the liquid will not be too close to the point where the glass is to be sealed together. This part of the operation is sometimes troublesome, but by tapping the tube and applying suction at either J or C, as required, the liquid can be adjusted exactly as desired. R is now closed and nitrogen admitted to tube T through J. The cell is now sealed off at D, and nitrogen admitted to the tube C. After the glass has cooled, the stopcock B is opened and the space above the developer is practically completely filled. The outer part of the electrode, between B, C and C', is not filled until after the next cell has been sealed on the apparatus and filled. As soon as the first cell has been sealed off, another is sealed on in its place, without in any way disturbing the content of tube T. The second cell is evacuated and filled with nitrogen twice through C, R is opened, the whole apparatus evacuated through C, and this cell rinsed and filled just as the first one was. After sealing this cell off, the remainder of the developer is poured out of the tube T and used to fill the tubes CC' of the two cells. The tube C is then plugged with filter paper, C' closed with rubber tubing and a glass plug, and the cells placed in the rack ready for measurements. The mixing apparatus can be used as often as desired, by sealing on new electrode cells.

With the use of the apparatus just described, seventeen electrode cells were filled for the investigation of eight different developers. Of these, only two cells containing amidol, and one containing hydrochinon with tetrathiourea ammonium bromide, appear to have come to equilibrium, although all have stood more than two and a half months. The amidol developer contained 100 g. sodium sulfite and 20 g. amidol dissolved in 1000 cc. water. The hydrochinon developer with thiourea was made according to the formula recommended¹ for the direct production of positives in the camera, and contained, dissolved in 1000 cc. water, 63 g. sodium sulfite, 126 g. sodium carbonate, 10.5 g. hydrochinon, and 0.5 g. tetrathiourea ammonium bromide.

At the end of a week, the amidol developer reached a point where it appeared to be in equilibrium, and both cells have, in fact, remained at about that value since. The average of ten readings from the two cells, extending over a month, is $+0.063$ volt, the extreme readings being $+0.057$ and $+0.067$ volt. One of the two cells containing the thiourea developer was found to have cracked where it was sealed off, and did not come to any equilibrium. The other reached the value -0.255 volt after eight days, maintaining this for a week (readings -0.255 , -0.251 , -0.253 , -0.260). When it was again read, three days later, it appeared to have approached a new equilibrium in the neighborhood of -0.150 volt. This was well maintained, as the readings over a period of six weeks show.

-0.148 , -0.157 , -0.162 , -0.125 , -0.144 ,

-0.120 , -0.148 , -0.154 , -0.154 .

It is well known that thiourea compounds are not very stable in alkaline solution; and it is not surprising, when we consider that the whole electrode cell contained only about 0.002 g. of this substance, that its action, while vigorous, was not prolonged; and that at the end of two weeks it appears to have been all decomposed. After this time the cell seems to have come to an equilibrium corresponding to the hydrochinon remaining. The average value for the equilibrium when thiourea was present is -0.254 volt; at the second stage, neglecting two values which are obviously irregularities, the average is -0.152 . The average for the Seed metol-hydrochinon developer previously determined (not made up *in vacuo*, page 2238) was -0.149 volt. This is the average of 19 readings from four cells, some of them covering a period of eighty days.

These two values for hydrochinon and metol-hydrochinon developers, respectively, are a good illustration of the fallacy of the direct comparison of single potentials. One would say from the single potentials that the

¹ Frary, Mitchell and Baker, *Proc. 8th Intern. Congr. Appl. Chem.*, 20, 141.

reducing powers of these developers were identical, although every photographer who has tried them knows that the metol-hydrochinon is much more rapid and apparently more vigorous in its action. By taking the hydrogen potentials and calculating the actual partial pressure of hydrogen, to which the developer is equivalent, as previously explained, we arrive at the relative reducing power of 2.7 : 1 (see Table I), which is photographically reasonable.

Mathews and Barmeier¹ stated that the potential did not change when the developer was made up from oxygen-free water in a vacuum. If this were true, it would upset all our theories, and leave us entirely in the dark as to the cause and nature of the single potentials observed. The procedure required for the use of the apparatus for sealing off the developer in an atmosphere free from oxygen, though slow and laborious, was adopted in order to be absolutely certain to exclude oxidation effects. In each of the seventeen electrodes sealed off in this way the potentials dropped, the curves being similar to those obtained in the presence of air. We are unable to account for the results claimed to have been obtained by Mathews and Barmeier. It will be seen that the oxygen in the water can not be the cause of the change in the electrode potential, while the theory of the production of hydrogen throughout the solution and its slow diffusion toward the electrode, and the presence of a reaction resistance depending on the nature of the reducing agent seem adequate to explain the changes observed.

In order to convert the values obtained for the single potentials of the developers into actual pressures of hydrogen, and so get a definite measure of the reducing power of these developers, it is necessary to determine the potential (E_{H_2}) which a platinized electrode saturated with hydrogen at atmospheric pressure will assume in the same solutions.

For all work on hydrogen potentials in this and the three following papers the form of apparatus shown in Fig. 7 was employed. This gives an electrode of simple construction and one with which reliable results to an accuracy of 0.0001 volt can be obtained. The hydrogen electrode has been thoroughly discussed by Loomis and Acree,² and a very extensive bibliography of the subject given.³ It was our experience that no form of electrode cell was reliable in which rubber stoppers were used, especially if the current of hydrogen stopped. By the use of the apparatus shown in the figure it is very often possible to maintain, at a constant temperature, a potential constant to 0.0001 volt with the hydrogen turned off, provided equilibrium has been previously reached.

¹ Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, 20, 201.

² *Am. Chem. J.*, 46, 585 (1911).

³ *Ibid.*, 46, 635 (1911).

A is the main electrode chamber, and E is the electrode of platinized platinum, having a short piece of platinum wire extending down from it as shown. The hydrogen enters at H and bubbles up through the solution to be investigated at D. The gas was made from c. p. sulfuric acid and arsenic-free zinc, and purified by passing through two small glass wash bottles containing acid potassium permanganate and a third flask containing a solution similar to that in the electrode cell itself. The gas leaves the apparatus through the trap K, which contains mercury, the height of which can be regulated by the reservoir M and pinchcock N.

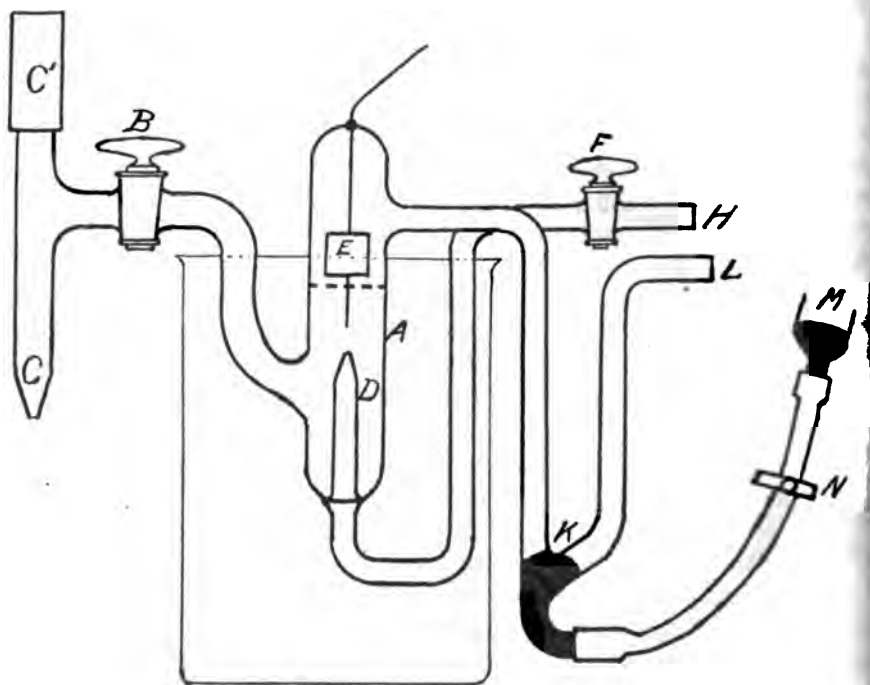


Fig. 7.—Hydrogen electrode.

The meniscus is so adjusted at the angle K that the gas pushes the mercury aside when under slight pressure, so the gas can escape but no air can enter. Connection with the intermediate liquid is made through the tube CC' as in previous cases. The height of the liquid should be about that indicated by the dotted line. It was found that equilibrium was reached more quickly if the electrode was shaken thoroughly with the solution before use, so as to be sure that the liquid had penetrated the pores of the platinum black. When the electrode was in good condition, the time required to reach equilibrium with a developer varied from four to fifteen minutes. As soon as one determination was completed

the cell was washed with hot water, filled with dilute sulfuric acid (1 : 20) and allowed to stand in this condition until again needed. The use of this acid assisted greatly in keeping the electrode in good condition and reduced the time required to reach equilibrium.

The temperature has a great influence on the hydrogen potential. This was controlled in our work by immersing the electrode cell in a beaker of water kept at 25°. The calomel electrode was also kept immersed in a water bath, so that its actual temperature could be readily determined and the appropriate correction made. The correction for barometric pressure was so small as to make it unnecessary to consider it.

In applying the hydrogen electrode to the problem of the reducing power of the developer, it is to be noted that the accuracy of the final result is no greater than that to which the single potential (E_x) of the developer can be determined. Since this can hardly be determined within less than a millivolt, a hydrogen potential of the same accuracy is sufficient. No difficulty was found in obtaining such accuracy, either with duplicate determinations from the same lot of solution, or with different lots made up from the same formula.

The hydrogen potential of the Seed metol-hydrochinon developer was determined at 23.5°, but its temperature coefficient was studied and found to be -0.0004 volt per degree. The value obtained at 23.5° was -0.3096 volt, which gives -0.3102 volt at 25°. Determination of the value of E_{H_2} for the amidol developer gave -0.031 volt and for the hydrochinon developer containing the thiourea salt -0.338 volt at 25°.

As previously shown (p. 2233), we can calculate the pressure of the hydrogen produced by the developer in equilibrium with the platinum electrode at 25° from the formula:

$$E = 0.05909 \log 1/C',$$

where $E = E_{H_2} - E_x$. The results for the developers which came to equilibrium are shown in Table I.

TABLE I.—REDUCING POWER OF DEVELOPERS.

Developer.	E_{H_2} .	E_x .	E .	C' (Atm.).	F.
Hydrochinon.....	-0.338	-0.152	0.186	0.000712	1.0
Metol-hydrochinon....	-0.310	-0.149	0.161	0.00188	2.7
Amidol.....	-0.031	+0.063	0.094	0.0257	36.0
Thiourea.....	-0.338	-0.254	0.084	0.0379	53.3

Under Column F are arranged numbers showing the relative reducing powers of the different developers, taking hydrochinon as unity. As previously stated, the values for thiourea and hydrochinon depend on only one cell, and may therefore be somewhat in error, but we feel that the absolute values for the amidol and metol developers of the formula given are quite well established.

For comparison with the above, the results obtained by Sheppard and Mees¹ are of interest. Recalculating them to a basis of hydrochinon = 1.0, their results show the relative reducing power of ferrous oxalate to be 1.6; that of hydroxylamine, 2.0; and that of *p*-aminophenol, 5.4. Their hydrochinon developer was made up with more than two molecules of sodium hydroxide to a molecule of hydrochinon, in order to have present the di-quinolate, which their work showed to have a greater reducing power than the mono-quinolate. As our results above are for a hydrochinon developer made up with carbonate, in which we have been able to show that the anion present is probably mono-quinolate, the value hydrochinon = 1.0 in our table probably represents a considerably smaller absolute reducing power than the same value in their results.

Photographically, it is well known that metol-hydrochinon is a much more rapid and powerful developer than hydrochinon alone. It is also known that the addition of thiourea compounds increases the reducing power of the developer to the point where it is capable of reducing unexposed silver bromide if a sufficient amount of alkali be present. With less alkali, little or none of the unexposed silver bromide is attacked, indicating that the reducing power of this developer is not so very far beyond the limits of ordinary developers. The figure 53.3 for the relative reducing power of the thiourea developer, as compared with hydrochinon, does not seem unreasonable. Amidol, thirty-six times as powerful a reducing agent as hydrochinon, is surprising, but not unreasonable photographically. It is well known that amidol is the only developer commonly used without alkali, that it brings up the image very quickly, and is very difficult to restrain with bromide. In the absence of alkali the gelatin must offer much more resistance to the development of the silver halide than it does with ordinary developers. Chemically, amidol would be expected to be more powerful than *p*-aminophenol, investigated by Sheppard and Mees, as it is a di-phenol and therefore much more subject to oxidation. When we note that amidol is only 13 times as powerful as metol-hydrochinon, and probably only three or four times as powerful as *p*-aminophenol (allowing for the difference in reducing power between our hydrochinon developer and that of Sheppard and Mees) and that both of the former require the use of alkalies in development, the figures above seem still more reasonable.

Summary and Conclusions.

1. The fundamental theory of the single potential of a developer and the conditions which retard the attainment of the equilibrium in its measurement have been discussed and illustrated.

¹ Sheppard and Mees, "Investigations of the Theory of the Photographic Process," pp. 188-196 (Longmans, Green & Co.).

2. The calculation of the partial pressure of hydrogen, to which the developer is equivalent, seems to be the only way in which the absolute or relative reducing power of developers can be directly measured.
3. The results obtained by the employment of this method seem to be photographically reasonable.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE HYDROGEN POTENTIALS OF SODIUM HYDROXIDE SOLUTIONS AND THE DISSOCIATION CONSTANT OF WATER.

By FRANCIS C. FRARY AND ADOLPH H. NIETZ.

Received July 28, 1915.

In connection with our work on the single potentials of developers, we noticed that the hydrogen potential (E_{H_2}) of a solution containing sodium carbonate and sulfite would change as much as thirty millivolts on adding the proper amount of hydrochinon to make a satisfactory developer. The change was in such a direction as to indicate that the hydrochinon combined with the sodium carbonate, forming a sodium salt and sodium bicarbonate, thereby decreasing the hydroxyl-ion concentration of the solution. It seemed that electrometric measurements of this nature might give us some very useful information about the reactions taking place when a developer is mixed, but in order to interpret such measurements we needed certain data not accessible in the literature.

It is evident that the mechanism of this reaction involves the hydrolysis of sodium carbonate and the reaction between the sodium hydroxide thus formed and the hydrochinon. As the sodium hydroxide is consumed, the hydrolysis must continue until the product of the bicarbonate concentration by the hydroxide concentration, divided by the concentration of the carbonate, reaches the value characteristic of the equilibrium at that temperature and dilution. In order to be able to determine the extent of the reaction, it is necessary to know both the hydrolysis constant of sodium carbonate and the hydrogen potentials corresponding to the various concentrations of sodium hydroxide. Since these were the fundamental quantities involved in the reaction under consideration, it appeared very desirable, in order to eliminate any errors inherent in the electrometric method, to use this method in their determination. As the hydrogen-ion concentration is the quantity directly susceptible of measurement by the electrometric method, it is first necessary to be able to transform a measurement of the hydrogen potential of the solution into terms of the concentration of sodium hydroxide.

A few measurements of the hydrogen potentials of sodium hydroxide

solutions have been made by Lorenz and Mohn,¹ but their values do not cover a sufficient range for our purpose, and nothing is stated as to the purity of their sodium hydroxide. Since a very small quantity of carbon dioxide can have a large effect in very weak sodium hydroxide solutions, we decided to repeat their work and extend it over a somewhat wider range.

A quantity of sodium amalgam was prepared by electrolysis of a strong solution of c. p. sodium carbonate, with a cathode of purified mercury. This amalgam was thoroughly washed with distilled water and then with conductivity water, and finally decomposed by treatment with conductivity water in the presence of platinum, in an aged Jena glass flask. Special precautions were always taken in the handling of this solution to avoid contamination by carbon dioxide. This solution, after preliminary titration and dilution, was standardized gravimetrically by evaporation in platinum with an excess of hydrochloric acid, and ignition of the resulting salt. The dilute solutions, made from this one by the addition of conductivity water, were all standardized in this way. All solutions were carefully preserved in Jena glass flasks which had been thoroughly aged by steam and the determinations were made as soon as possible after mixing, to avoid contamination by the glass.

The hydrogen electrode described in the previous paper (p. 2244) was used, and all determinations were made at 25°. The results in Table I are each the mean of a number of concordant measurements, using a normal calomel electrode and a saturated solution of potassium chloride as the intermediate liquid.

TABLE I.—HYDROGEN POTENTIALS OF PURE SODIUM HYDROXIDE SOLUTIONS.

E_{H_2} is the observed potential referred to the normal calomel electrode as $+0.560 \pm 0.0006$ ($t = 18$), E_h is the same potential on the hydrogen scale.

Sodium hydroxide conc.		E_{H_2}	E_h
Mols per liter.	Liters per mol.		
1.000	1.0	-0.525	-0.807
0.507	1.97	-0.506	-0.788
0.2039	4.91	-0.484	-0.766
0.102	9.8	-0.470	-0.752
0.01057	94.6	-0.413	-0.695
0.00078	1282.0	-0.344	-0.626

In all cases the potentials listed are on the basis of the potential of the electrode minus the potential of the solution. In order to convert E_{H_2} into the values for E_h , it is necessary, according to the work of Loomis and Acree,² to add -0.282 volt, and the resulting values are listed under E_h in the table. Since the basis of the hydrogen scale is the hydrogen

¹ *Z. physik. Chem.*, 60, 422 (1907).

² *Am. Chem. J.*, 46, 634 (1911).

potential of a solution which is normal in respect to the hydrogen ion, E_h represents in each case the e. m. f. between a hydrogen electrode in a solution of normal hydrogen-ion concentration and a hydrogen electrode in the given solution.

It is evident that from these results we may calculate directly the hydrogen-ion concentration in the sodium hydroxide solutions by means of the formula

$$E_h = 0.05909 \log 1/c',$$

where c' represents the hydrogen-ion concentration in the sodium hydroxide solution at 25°.

In order to convert these values into the corresponding concentrations of the hydroxyl ion, it is only necessary to know the dissociation constant of water. It is obvious that this constant will be involved in every measurement of the hydrolysis of sodium carbonate, and in all other measurements of the alkalinity of a solution. The hydroxyl-ion concentration of any pure sodium hydroxide solution can easily be determined from its degree of dissociation as indicated by conductivity measurements, which have been very accurately made by various authors. To determine k_w , the dissociation constant of water, it is only necessary to substitute in the above equation the value of $c' = k_w/[\text{OH}^-]$, giving us

$$E_h = 0.05909 \log [\text{OH}^-]/k_w.$$

The conductivity data used for the calculation of the dissociation of the sodium hydroxide, with their sources, are shown in Table II.

TABLE II.—CONDUCTIVITY OF SODIUM HYDROXIDE SOLUTIONS AT 18°.

v (liters per gram-equivalent).	λ_p at 18.	Determined by	v (liters per gram-equivalent).	λ_p at 18.	Determined by
1	157.0	Foster ¹	200	203	Kohlrausch ²
2	174.1	Foster ¹	500	204.5	Foster
10	195.4	Foster ¹	1000	208	Kohlrausch
50	197	Kohlrausch ²	5	210 ³	Goldsmith and Larsen ⁴
100	200	Kohlrausch ²			

Arrhenius⁵ gives the temperature coefficients of the conductivity of sodium hydroxide for temperatures between 18° and 40° as 0.0202 for $v = 2$ and $v = 10$, and 0.0213 for $v = 100$. No more complete data on temperature coefficients has been found, and most of the work on the conductivity of sodium hydroxide appears to have been done at 18°. We have therefore calculated the conductivity and degree of ionization from the above values. The results so obtained are undoubtedly a very

¹ *Phys. Rev.*, 8, 257 (1899).

² Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 160.

³ At 25°.

⁴ *Z. physik. Chem.*, 71, 453 (1910).

⁵ *Ibid.*, 9, 339 (1892).

close approximation, and when the dissociation is plotted as a function of the dilution a smooth curve is obtained.

Recent determinations of the conductivity of the ions give, for 25° , $\text{Na}^+ = 50.5$, $\text{OH}^- = 196$, from which the equivalent conductivity of sodium hydroxide at infinite dilution is 246.5. Table III shows the ionization as calculated from the figures in Table II; the temperature coefficients c and the value for $\lambda_\infty = 246.5$.

TABLE III.—IONIZATION OF SODIUM HYDROXIDE AT 25° .

v .	λ_v at 18° .	c .	λ_v at 25° .	$\alpha = \lambda_v/\lambda_\infty$.
1	157.0	0.0202	179.2	0.727
2	174.1	0.0202	198.7	0.806
5	210.3	0.853
10	195.4	0.0202	223.0	0.905
100	200	0.0213	230.0	0.933
200	203	0.0215	233.6	0.948
500	204.5	0.0215	235.3	0.955
1000	208	0.0215	239.3	0.971

α represents the fraction ionized. These results were carefully plotted on a large scale, so that interpolation from the curve would be as close as the above values would warrant. We assume complete ionization at $v = 2000$. The curve also indicates this.

Applying the above data to our determinations of the hydrogen potentials, we obtain the results shown in Table IV.

TABLE IV.

Ionization constant of water in the presence of sodium hydroxide, and the hydrogen potentials corresponding to various hydroxyl-ion concentrations in sodium hydroxide solutions. Concentrations in gram-molecules or gram-ions per liter.

NaOH.	α .	OH.	E_h .	$k_w \times 10^4$.
1.000	0.727	0.727	-0.807	1.60
0.507	0.805	0.408	-0.788	1.88
0.2039	0.852	0.1737	-0.766	1.89
0.102	0.9025	0.0920	-0.752	1.73
0.01057	0.933	0.00986	-0.695	1.71
0.00078	0.983	0.0007667	-0.626	1.95

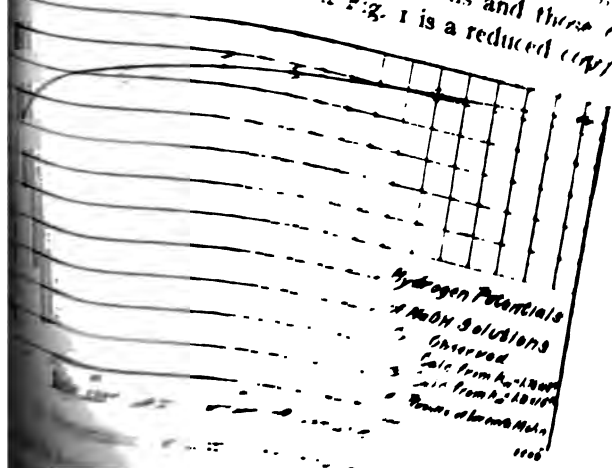
We feel justified in omitting the last value from the average for k_w , on account of the difficulty of making accurate determinations in such dilute solutions, and the relative size of the error introduced by a small unavoidable absorption of carbon dioxide. The average of the first five values gives $k_w = 1.76 \times 10^{-14}$ at 25° .

Considerable work has been done on the dissociation of water, both by conductivity methods, methods depending on hydrolysis of complex salts, and by measurement of potentials in the acid-alkali cell. Ostwald¹ made use of the acid-alkali cell as early as 1893, but his results have since

¹ *Z. physik. Chem.*, 11, 521 (1893).

superseded by other determinations. Lorenz and Ishii,¹ in 1930, determined for k_w at 25° the value 1.21×10^{-14} . Löwenherz,² in 1931, determined for 0.1 N acid and alkali the value 1.4×10^{-14} and for 0.01 N acid and alkali the value 1.4×10^{-14} . The lowest value at this temperature appears to be that of Kanda (1937), who obtained by the hydrolysis of a complex organic salt, in 0.1 M solution, Löwenherz's value 1.42×10^{-14} is the highest found in the literature. Although Wijs³ obtained 1.4×10^{-14} for the catalysis of water by water.

At 25° the value for k_w is somewhat higher than the value 1.2×10^{-14} , the fact that concordant results were obtained over a wide range of dilutions indicates that the same mechanism is the controlling factor in which the behavior of such strong electrolytes is concerned. If there is any interaction between the water and the calomel electrode, it is included in our determinations and these are not to be surprising if their presence causes a shift in the potential of the water. The hydrogen potentials are calculated from the observed data and plotted in Fig. 1 is a reduced copy of the original data.



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present, we need to know the extent to which it is dissociated in the presence of the sodium carbonate. It seems to be well established¹ that in a solution containing two salts having a common ion, each is dissociated to the same extent that it would be in a solution having the same concentration of the common ion. In this case the concentration of the common ion (sodium) is fixed by the dissociation of the sodium carbonate. From the data of Kohlrausch,² and Jones and West,³ we constructed a curve from which the dissociation of sodium carbonate at any concentration could be determined by inspection, and have used the values of the sodium ion thus obtained in correcting for the repression of the ionization of the sodium hydroxide.

The carbonate used was prepared by heating a sample of c. p. sodium bicarbonate for an hour at 300° in an electric oven. From this a twice molar solution was made and diluted with conductivity water to the concentrations desired. It was found that if ordinary distilled water was used, especially for the more dilute solutions, irregular and false results were obtained, apparently on account of its carbon dioxide content. The hydrogen electrodes described in our paper on the single potentials of developers were used in this work, the temperature being maintained at 25° by immersion in water, and other precautions taken as previously mentioned in the paper referred to.

The results are shown in Table I. To determine the corrected sodium hydroxide concentration from the observed hydrogen potential on the hydrogen scale (E_h), the first step is to determine, from the curve described in our previous paper, the concentration of pure sodium hydroxide which would give this potential. From the curve showing the dissociation of sodium hydroxide we determine α at this concentration, and by multiplying this value by the concentration, obtain the concentration of the hydroxyl ion in the solution measured. From the curve showing the dissociation of sodium carbonate we determine α and the total concentration of sodium ion in the solution. From the curve showing the dissociation of sodium hydroxide, we now find by trial the concentration of pure sodium hydroxide which would furnish the same concentration of the sodium ion, and record α , the degree of dissociation at that concentration. As previously explained, this is the degree of dissociation of the sodium hydroxide present in the sodium carbonate solution, and by dividing the concentration of the hydroxyl ion by this figure we obtain the corrected sodium hydroxide concentration. K is then equal to the square of this concentration divided by the difference between this and the original

¹ Bray and Hunt, *THIS JOURNAL*, 33, 681 (1911); Arrhenius, *Z. physik. Chem.*, 2, 184 (1887); 31, 204 (1899).

² Landolt-Börnstein Tabellen, 4th ed., p. 1124.

³ *Am. Chem. J.*, 34, 357 (1905).

TABLE I.—HYDROLYSIS OF SODIUM CARBONATE IN SOLUTION AT 25°.

Strength of soln. Molar.	ρ .	R_H .	R_p .	ρ .	Conc. NaOH calc. from R_p .	α .	Apparent OH ⁻ conc.	α for Na ₂ CO ₃ at given dilution.	Corresp. Na ⁺ conc.	NaOH conc. furnish- ing same Na ⁺ conc.	α for NaOH.	Corr. NaOH conc.	$\lambda \times 10^4$.
2.0	0.5	-0.402	-0.684	152	0.00658	0.937	0.00616	0.174	0.696	0.940	0.738	0.00835	3.50
1.5	0.67	-0.398	-0.680	175	0.0057	0.938	0.00535	0.24	0.72	0.988	0.728	0.00735	3.62
1.0	1.0	-0.395	-0.677	200	0.00500	0.94	0.00470	0.31	0.62	0.81	0.758	0.00620	3.9
0.708 ¹	1.41	-0.393	-0.675	215	0.00465	0.941	0.00437	0.355	0.504	0.64	0.784	0.00558	4.45
0.5	2	-0.390	-0.672	240	0.00417	0.943	0.00393	0.39	0.39	0.49	0.807	0.00487	4.8
0.2	5	-0.384	-0.666	300	0.00333	0.946	0.00315	0.47	0.188	0.22	0.849	0.00371	7.0
0.1	10	-0.379	-0.661	360	0.00278	0.949	0.00264	0.54	0.108	0.12	0.889	0.00297	9.1
0.05	20	-0.373	-0.655	450	0.00222	0.952	0.00211	0.60	0.060	0.0655	0.916	0.00230	11.1
0.02	50	-0.364	-0.646	625	0.00160	0.959	0.00153	0.673	0.027	0.029	0.926	0.00165	14.8
0.01	100	-0.358	-0.640	790	0.00127	0.967	0.00123	0.717	0.0143	0.0154	0.931	0.00132	17.6
0.005	200	-0.349	-0.631	1160	0.000862	0.977	0.000842	0.75	0.0075	0.0081	0.935	0.00090	19.7

¹ C. P. Na₂CO₃ dried at 300°, used for this instead of the carbonate prepared from the bicarbonate.

concentration of sodium carbonate, since obviously the concentration of the bicarbonate is the same as that of the hydroxide, while the final carbonate concentration is the original concentration minus the portion hydrolyzed.

By recalculating the results of Auerbach and Pick, according to the above-described method, for K , we obtained Table II.

TABLE II.

Hydrolysis of sodium carbonate in solution at 25°, from results of Auerbach and Pick. Concentrations expressed in gram-molecules and gram-ions per liter.

Observed concentrations.		Corr. NaOH conc.	$K \times 10^4$.
Na_2CO_3 .	OH^- .		
0.2	0.0034	0.004	8.16
0.1	0.0029	0.00326	11.0
0.05	0.0023	0.0025	13.1
0.01	0.00113	0.00122	17.0
0.005	0.00080	0.000856	17.7
0.001	0.00034	0.000355	19.5

Comparing the values of K in Tables I and II, for the range common to both, it will be noticed that the agreement is as good as could be expected, especially since Auerbach and Pick used a colorimetric method depending on an electrometric determination of the hydroxyl-ion concentration in a series of known solutions according to the method of Sørensen.¹

As previously stated, the value of k_4 is the limiting value for K , since it represents the ionic equilibrium involved. It is obvious that the values of K should approach k_4 at infinite dilution, where the substances concerned are completely dissociated, but they should not approach it at dilutions where the dissociation of any one of the constituents is far from complete. Assuming the value of 1.12×10^{-14} for k_w , the dissociation constant of water at 25°, Auerbach and Pick calculate for k_4 the value 19×10^{-5} . By reference to Table II, it will be seen that the value of K calculated from their work, which should approach this value as a limit, already exceeds it in solutions 0.001 molar in respect to sodium carbonate, where this salt is only about 80% dissociated and sodium hydroxide only 96%. Little is known of the dissociation of the bicarbonate, but it would certainly be less than that of the hydroxide. According to our results (Table I), K exceeds 19×10^{-5} for 0.005 molar carbonate solution, where the carbonate is only 75% dissociated. If we assume that the dissociation constant of water in the presence of sodium hydroxide is 1.76×10^{-14} at 25°, as determined in our previous paper, the value of k_4 becomes 28×10^{-5} , which appears much more reasonable as a limiting value for K , particularly if the values of K at various dilutions be plotted and the slope of the curve observed. The work of Auerbach and Pick therefore confirms ours over part of the range investigated.

¹ *Biochem. Z.*, 21, 131 (1909); 22, 352 (1909); 24, 381, 387 (1910).

for the values of K , and furnishes additional evidence of the trustworthiness of a higher value for the dissociation constant of water in the presence of sodium hydroxide than the one generally accepted.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE REACTION BETWEEN ALKALIES AND METOL AND HYDROCHINON IN PHOTOGRAPHIC DEVELOPERS.

BY FRANCIS C. FRARY AND ADOLPH H. NIETZ.

Received July 28, 1915.

In our paper on the single potential of developers, we have mentioned noticing that the addition of hydrochinon caused a change of thirty millivolts in the hydrogen potential of a solution containing sodium carbonate and sodium sulfite. As this seemed to indicate a combination between the alkali and the reducing agent, it appeared possible to use these hydrogen potentials as a means of studying the reactions which take place when a developer is mixed. After determining the hydrogen potentials of pure solutions of sodium hydroxide and the hydrolysis constant of sodium carbonate, as described in our previous papers, we have the necessary information upon which to base our calculations of the reactions involved.

In this study we investigated four different hydrochinon developers, seven solutions of sodium hydroxide and hydrochinon, and one solution containing metol and sodium hydroxide. The composition of the developers is shown in Table I.

TABLE I.—COMPOSITION OF DEVELOPERS, GRAMS PER 1000 CC. WATER.

Dev. No.	Hydrochinon.	Sodium sulfite.	Sodium carbonate.
1	11.1	7.8	141.7
2	7.0	50.0	150.0
3	7.0	50.0	75.0
4	7.0	None	75.0

The sulfite used was an analyzed anhydrous article, and the carbonate was prepared by drying the last c. p. salt at 300°. In making a determination the hydrogen potential of the solution containing all the constituents except the metol and hydrochinon was first found as described in our previous papers. Then the complete developer was tested in the same way. Where the solution contained only sodium hydroxide and hydrochinon (or metol), reference to the curve showing the hydrogen potentials of solutions of pure sodium hydroxide gave us directly the concentration of the sodium hydroxide before and after adding the reducing agent. From the difference between these two values the amount of sodium hydroxide used up could be readily calculated.

Where sodium carbonate was present, reference to the curves for the hydrogen potentials of sodium hydroxide solutions and for their dissociation gives us the hydroxyl-ion concentration corresponding to the potentials observed. It is next necessary to make corrections for the effect of the sodium carbonate and sulfite in repressing the dissociation of the hydroxide. Comparison of the data on the dissociation of these two salts showed that, over the range under consideration, sodium sulfite was about 10% more dissociated than the carbonate. The simplest way of obtaining the probable total sodium-ion concentration appeared to be to consider the sulfite equivalent to 10% more than its own molarity of the carbonate, add this quantity to the actual molarity of the carbonate, and from the curve determine the degree of dissociation of the carbonate at that dilution, and thus the total sodium-ion concentration. On the assumption, then, that in a solution of two salts having a common ion, each is dissociated to the same extent that it would be if it were present alone in a solution having the same concentration of this common ion, the degree of dissociation of the sodium hydroxide, as repressed by the carbonate and sulfite present, can be calculated as explained in the previous paper.

Having obtained the corrected concentration of the sodium hydroxide before and after the addition of the hydrochinon, it is evident that the sodium hydroxide which has been used up by the hydrochinon consists of two parts: one represented directly by the difference in the concentrations of the hydroxide before and after adding the hydrochinon, and the other corresponding to the amount of bicarbonate formed on the addition of the hydrochinon, due to the progressive hydrolysis as the sodium hydroxide concentration decreases. This formation of the bicarbonate furnishes the greater portion of the hydroxide used up, and is determined from the constant for the equilibrium

$$K = \frac{[\text{NaOH}] [\text{NaHCO}_3]}{[\text{Na}_2\text{CO}_3]}$$

for the given dilution. The values of this constant, as determined in the previous paper, were plotted as functions of the concentration, and formed a smooth curve. From this curve the value of K for any dilution can be determined by inspection. Substituting in this equation the net concentration of the carbonate and the corrected concentration of the sodium hydroxide at any time, we can find the amount of sodium bicarbonate present in the solution. The amount of hydroxide used up during the hydrolysis is evidently equivalent to the difference in the concentrations of the bicarbonate before and after adding the hydrochinon. By the net carbonate concentration, we understand the difference between the original concentration of carbonate and the amount hydrolyzed. By making a preliminary calculation from the corrected concentration

TABLE II.
Reactions between sodium carbonate, sodium sulfite, and hydrochinon. Salt concentrations expressed in mols per liter, ionic concentrations in gram-ions per liter.

Developer:	Composition.					Total equiv.	α for this Total Na ⁺ .	Corresp. NaOH conc.	Obs. OH ⁻ .	Corr. NaOH.	K X 10 ⁴ .	On adding hydrochinon.			Mols NaOH per mol hydro- chinon.
	Na ₂ CO ₃ .	Na ₂ SO ₃ .	Na ₂ CO ₃ .	Na ₂ CO ₃ .	Decrease NaOH.							Increase NaHCO ₃ .	Total NaOH consumed.	Conc. hydro- chinon.	
1 (before)	1.337	0.062	1.40	0.25	0.70	0.95	0.735	0.00109	0.00148	3.7	0.0010	0.0624	0.0634	0.101	0.63
1 (after)	1.337	0.062	1.40	0.25	0.70	0.95	0.735	0.00033	0.00045	3.7	0.0010	0.0624	0.0634	0.101	0.63
2 (before)	1.415	0.40	1.85	0.20	0.74	1.02	0.725	0.00669	0.00922	3.7	0.0081	0.0438	0.0519	0.064	0.81
2 (after)	1.415	0.40	1.85	0.20	0.74	1.02	0.725	0.00081	0.00112	3.7	0.0081	0.0438	0.0519	0.064	0.81
3 (before)	0.708	0.40	1.15	0.29	0.667	0.89	0.745	0.00360	0.00483	4.3	0.0040	0.0274	0.0314	0.064	0.49
3 (after)	0.708	0.40	1.15	0.29	0.667	0.89	0.745	0.00061	0.00082	4.3	0.0040	0.0274	0.0314	0.064	0.49
4 (before)	0.708	None	0.708	0.555	0.503	0.64	0.784	0.00437	0.00558	4.3	0.0042	0.0469	0.0511	0.064	0.92
4 (after)	0.708	None	0.708	0.555	0.503	0.64	0.784	0.00050	0.00063	4.3	0.0042	0.0469	0.0511	0.064	0.92

of the sodium hydroxide, using the figure for the original concentration of the carbonate, the approximate amount (molarity) of bicarbonate formed can be determined. Subtracting this from the original carbonate value gives a very close approximation of the net carbonate, from which a final figure for the bicarbonate can usually be obtained.

From the total bicarbonate formed during the hydrolysis, plus the direct loss of the hydroxide concentration, the total amount of sodium hydroxide which has combined with the hydrochinon is easily determined, and can be compared with the amount of hydrochinon present.

We have carried out this determination on the four developers shown in Table I, with the results shown in Table II. It will be noticed, that, strictly speaking, No. 4 is not a developer since it contains no sulfite. It was included for the purpose of showing more clearly the effect of the sulfite.

Since Sheppard and Mees,¹ in their work on hydrochinon developers, used sodium hydroxide instead of the carbonate, and found that the velocity of development was a maximum when approximately two molecules of the hydroxide were present for one molecule of hydrochinon, and thus concluded that the active developing agent was the anion of the diquinolate,—we undertook a series of measurements on mixtures of various proportions of hydrochinon and sodium hydroxide, without sulfite, in order to determine whether under other conditions the diquinolate was formed. These results are presented in Table III.

TABLE III.

Reaction between hydrochinon and metol and sodium hydroxide. Concentrations all expressed as gram-molecules per liter. Determination below dotted line is metol and sodium hydroxide, without hydrochinon.

Orig. conc. NaOH.	Conc. hydrochinon added.	NaOH: hydrochinon as mixed.	Final conc. NaOH.	Loss of conc. NaOH.	Mols NaOH comb. one mol hydrochinon.
0.102	0.0273	3.74	0.0432	0.059	2.14
0.0103	0.00364	2.83	0.00278	0.0075	2.06
0.103	0.0509	2.02	0.0144	0.0884	1.73
0.103	0.0545	1.89	0.01087	0.0920	1.72
0.0103	0.00636	1.62	0.00148	0.0088	1.38
0.0103	0.01	1.03	0.000495	0.0098	0.98
0.0103	0.0109	0.945	0.00046	0.0098	0.90
...
	(Metol)	(Metol)			(Metol)
0.0103	0.0029	3.56	0.0016	0.0087	3.00

It will be noticed from this table that, by varying the proportions of hydrochinon and alkali, either the mono- or diquinolate or mixtures of the two can be formed, as would be expected; and that in both cases the solution is still alkaline; even though, in the last solution in the table

¹ "Investigations of the Photographic Process," p. 176.

(above the dotted line), there is an excess of hydrochinon over the amount required to form the monoquinolate. As would be expected, the ratio of the constituents, the alkalinity of the final solution, and the dilution seem to be the factors which decide the extent to which the two substances combine; in other words, there is the expected tendency toward hydrolysis of both the mono- and diquinolates, and the tendency of the diquinolate to hydrolyze is evidently greater than that of the monoquinolate. The last two results are especially interesting, as it will be noticed that the alkalinity of the final solution is about the same as that found in the carbonate solution (Developer No. 4, Table II). The proportion of the hydrochinon combined with the alkali in the two cases checks as well as could be expected, considering the difference in the concentration of the hydrochinon, and bears out the theory that in ordinary hydrochinon developers, made up with sodium carbonate, the anion of the monoquinolate is probably the principal developing agent.

Another very interesting conclusion which can be drawn from Table II relates to the role of the sulfite. A study of the number of mols of sodium hydroxide consumed per mol of hydrochinon, makes it appear very probable that the sulfite combines with some of the hydrochinon, and that the sulfite and hydroxide divide the hydrochinon between them, according to some definite law. It will be noted that Developers 3 and 4 are the same, except that the sulfite is omitted in No. 4. In the latter, apparently 92% of the hydrochinon has combined with the alkali (assuming the formation of the monoquinolate), and 8% is free. Upon now adding sulfite so that the concentration of the latter is 0.40 molar (Developer No. 3), we find that only 49% of the hydrochinon remains combined with the hydroxide, although the developer is now more alkaline than it was before adding the sulfite (0.00082 *N* in free sodium hydroxide as compared with 0.00063). Upon doubling the concentration of the carbonate (Developer No. 2) the proportion of the hydrochinon combined with the alkali rises to 81%, but does not reach the value for Developer No. 4, where the sulfite is absent, although the final alkali concentration of the developer has nearly doubled (0.00112 as compared with 0.00063). Developer No. 1 has nearly twice the hydrochinon concentration of the others, about the same carbonate as No. 2, but only about one-sixth as much sulfite. The final alkalinity is the lowest of all, the developer being only 0.00033 *N* in hydroxyl ion and 0.00045 *N* in sodium hydroxide; the larger proportion of the hydrochinon increases the proportion of this substance which does not combine with the hydroxide, but which at least partly combines with the sulfite. The phenomena are easily explained upon the basis of the following equations showing the probable equilibria:

$$K_1 = \frac{[C_6H_4(OH)_2][NaOH]}{[C_6H_4OHONa]}$$

$$K_2 = \frac{[\text{C}_6\text{H}_4\text{OHONa}][\text{NaOH}]}{[\text{C}_6\text{H}_4(\text{ONa})_2]}$$

$$K_3 = \frac{[\text{C}_6\text{H}_4(\text{OH})_2][\text{Na}_2\text{SO}_3]}{[\text{C}_6\text{H}_4(\text{OH})_2\text{Na}_2\text{SO}_3]}$$

The formula for the addition compound with sodium sulfite is not known, but is assumed for purposes of illustration. From our result it would appear that K_2 is greater than K_3 , and this in turn much greater than K_1 , which would make the monoquinolate the most stable substance of the three.

In connection with the hydrochinon developer, a very interesting observation was made and is mentioned in our paper on the single potentials of developers. The hydrogen potential of a part of a sample of Developer No. 1 was taken, air was then bubbled through the rest of the sample for three hours and it was allowed to stand exposed to the air for four hours more. Upon taking the hydrogen potential of this oxidized developer (now deep brown in color), it was found to be identical with the original value. This developer was then allowed to stand exposed to the air all night, and the potential again taken. The value was still the same as that of the original fresh developer. It would appear then, that the oxidation of such a developer, even though carried as far as it could be, does not change its alkalinity, *i. e.*, does not form any new compounds of an acidic nature.

One experiment was made with some of Hauff's metol, and is shown at the bottom of Table III, separated from the hydrochinon results by a dotted line. Assuming the formula, $\text{HO.C}_6\text{H}_4\text{—NHCH}_3 \cdot \frac{1}{2}\text{H}_2\text{SO}_4$, as stated by Sheppard and Mees¹ with a molecular weight of 172, the surprising result is obtained that three molecules of sodium hydroxide can combine with one molecule of metol. One of these apparently removes the half molecule of sulfuric acid, another unites with the OH group, while the third may have replaced the sulfuric acid in its combination with the $\text{CH}_3\text{NH—}$ group. Further work of this sort on developing agents should produce much valuable information, and we believe that the results presented herewith indicate a suitable method for such work.

Summary and Conclusions.

1. It is possible by electrometric measurements to determine the reactions between some of the constituents of a developer, using our values for the hydrogen potentials of pure sodium hydroxide solutions and for the hydrolysis constant of sodium carbonate.
2. Such studies indicate that sodium hydroxide and hydrochinon can form either mono- or diquinolates, according to the conditions.
3. It appears that with sodium carbonate and hydrochinon, in the

¹ "Investigations of the Photographic Process," p. 187.

concentrations usually used for developers, most of the hydrochinon would unite with the alkali to form the monoquinolate if the sulfite were not present.

4. When sulfite and carbonate are both present, they appear to divide the hydrochinon between them.

5. Complete oxidation of a hydrochinon developer may be accomplished without changing its alkalinity.

6. One molecule of metol appears to be capable of combining with three molecules of sodium hydroxide, in the absence of a sulfite.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY.]

REACTIONS IN LIQUID AMMONIA. II.

1. THE ACTION OF ACID AMIDES ON THE AMIDES, IMIDES AND NITRIDES OF CERTAIN HEAVY METALS. 2. METALLIC SALTS OF ACID AMMONO ESTERS.

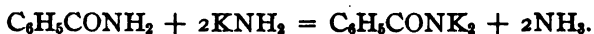
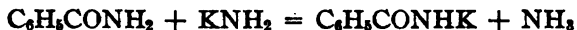
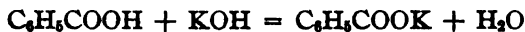
BY EDWARD C. FRANKLIN.

Received July 8, 1915.

Introduction.

Some years ago Franklin and Stafford¹ found that certain acid amides and potassium amide react with each other, when dissolved in liquid ammonia, in a manner strikingly similar to the familiar interaction of acids and bases in aqueous solutions.

Typical examples of such analogous reactions are represented by the equations,



The first equation represents the action of an aquo acid on an aquo base to form an aquo salt, the second and third, the action of an ammono acid on an ammono base to form ammono salts.

In view of the analogies thus indicated, and of others given in detail elsewhere,² the writer has long had in mind attempts to prepare ammono salts of some of the heavier metals by the action of liquid ammonia solutions of ammono acids on the insoluble amides, imides or nitrides of the metals. Such reactions are, of course, in principle not different from those studied by Franklin and Stafford referred to above, but at the same time it is interesting and important to show that salts of the heavy metals may be prepared in this way.

The amide of silver,³ the imides of lead¹ and copper⁴ and the nitride of

¹ *Am. Chem. J.*, 28, 95 (1902).

² *Ibid.*, 47, 285 (1912).

³ *THIS JOURNAL*, 27, 833 (1905).

⁴ *Ibid.*, 29, 656 (1907).

thallium,¹ since they may be readily prepared in a pure state, were chosen as insoluble bases, while acetamide, benzenesulfonamide and *p*-toluenesulfonamide—the one a very weak and the other two much stronger ammono acids—were the acids conveniently at hand for use in the experiments to be described. Mercuric nitride, although easily prepared² in a state of purity, was not used for the reason that mercuric salts of the acid amides are readily formed in aqueous solution and as a consequence are already known in large number. That they may be as readily prepared from liquid ammonia solutions is practically certain.

Ammono Salts of Certain Heavy Metals.

The silver amide, cuprous and lead imides and thalious nitride used in the experiments described below were obtained pure by thoroughly washing the precipitates formed by the action of potassium amide upon liquid ammonia solutions of soluble salts of the respective metals. Since, however, the manipulative details whereby these substances may be prepared have already been published³ it is unnecessary to repeat a description of them here.

Silver Ammonoacetate,⁴ CH_3CONHAg , and the Diammonate, $\text{CH}_3\text{CONHAg} \cdot 2\text{NH}_3$.—When a solution of acetamide in liquid ammonia is poured upon silver amide, prepared by the interaction of approximately equivalent quantities of potassium amide and silver nitrate, the ammono base dissolves to a clear, colorless solution. After proper adjustment of the concentration of the solution thus formed, a crop of beautiful crystals separates when the solution is cooled in a bath of liquid ammonia. A product, obtained in the manner thus described, was recrystallized twice from pure ammonia distilled over from the second leg of the reaction tube. When, however, the attempt was made to dissolve the crystals a third time they disintegrated to a smeary mass which clung to the walls of the reaction tube and refused to go into solution, but which became crystalline again on evaporating off the greater portion of the solvent. In view of the fact that acetamide is a very weak acid, it may be concluded that this behavior of the salt is indicative of ammonolysis in the manner represented by the equation $\text{CH}_3\text{CONHAg} + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CONH}_2 + \text{AgNH}_2$.

Preparatory to analysis the specimen of well crystallized salt was exposed over night to the action of water vapor, then dissolved in dilute sulfuric acid and removed from the reaction tube after the manner described in the papers referred to above. The silver in an aliquot part

¹ *J. Phys. Chem.*, 16, 683 (1912).

² *THIS JOURNAL*, 27, 835 (1905).

³ *Loc. cit.*

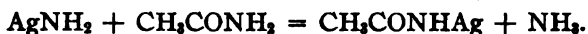
⁴ Strecker, many years ago (*Ann. Chem.*, 103, 324 (1857)), obtained acetamide silver as crystalline scales (Schuppen) from a solution formed by dissolving freshly precipitated silver oxide in aqueous acetamide.

of the solution was determined as the chloride, the nitrogen in another portion by the method of Kjeldahl.

The specimen, dried in vacuum at 20°, weighed 0.2926 g. One-half gave 0.1054 g. AgCl and two-tenths gave 0.0124 g. N.

Calc. for $\text{CH}_3\text{CONHAg} \cdot 2\text{NH}_3$: Ag, 54.0, N, 21.0; found: 54.2 and 21.2.

Silver ammonoacetate is, therefore, shown to be formed by the action of acetamide on silver amide in accordance with the equation



The salt is fairly soluble in liquid ammonia and separates from cold, concentrated solutions in the form of beautiful crystals containing two molecules of ammonia.

Thallous Ammonoacetate, CH_3CONHTl , and the Diammonate, $\text{CH}_3\text{CONHTl} \cdot 2\text{NH}_3$.—Thallium nitride, which is precipitated when thallium nitrate and potassium amide are brought together in liquid ammonia solution, dissolves readily in a solution of acetamide to form a salt which separates in the form of well developed crystals when the fairly concentrated solution is cooled to a low temperature.

Preparation I.—The nitride obtained from 1.33 g. of thallous nitrate was treated with a liquid ammonia solution of one equivalent of acetamide. The solution of acetamide thallium formed was decanted from a small quantity of undissolved thallium nitride, concentrated and cooled until a crop of crystals was obtained. The specimen of salt was then recrystallized twice, hydrolyzed by water vapor and dissolved in dilute sulfuric acid preparatory to removal from the reaction tube for analysis. The thallium in a portion of the solution was determined as the iodide, the nitrogen in another portion by the method of Kjeldahl.

Dried in vacuum at 120° the specimen weighed 0.9258 g. One-half gave 0.5683 g. TlI, the other half gave 0.0248 g. N.

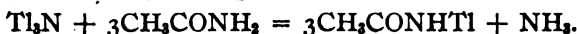
Preparation II.—The thallium nitride from 1.33 g. of thallous nitrate was treated with a considerable excess of acetamide, with the result that the precipitate was completely dissolved. Otherwise this experiment was a duplicate of the preceding.

Dried in vacuum at -40°, the specimen weighed 1.0406 g. Dried at 120°, it weighed 0.9212 g. One-half of the specimen after heating to the latter temperature gave 0.0246 g. N. Four-tenths gave 0.4604 g. TlI.

Calc. for $\text{CH}_3\text{CONHTl} \cdot \text{Ti}$ 77.8, N 5.4; found: (I) 75.8¹ and 5.4; (II) 77.1 and 5.4.

Calc. for $\text{CH}_3\text{CONHTl} \cdot 2\text{NH}_3$: 2NH₃ 11.5; found: 11.5.

The action of a liquid ammonia solution of acetamide on thallous nitride is, therefore, represented by the equation



¹ The low weight of the thallium iodide is probably explained by the fact that the weighing of the prepared Gooch crucible was inadvertently omitted and as a result the weight of the thallium iodide was taken as the loss on ignition.

The salt is very soluble in liquid ammonia at laboratory temperatures but is much less soluble at lower temperatures. It separates from solution in the form of beautiful, colorless crystals, containing two molecules of ammonia of crystallization, which as they approach laboratory temperature, melt and give off ammonia. At 120° the removal of ammonia is complete and at the same time a small quantity of sublimate, presumably acetamide resulting from the ammonolysis of the salt, appears in the upper cooler portion of the specimen tube. It is interesting to note that the least trace of air gaining entrance to the tube causes a blackening of the salt in a manner similar to that observed in the case of potassium ammoniothallite.¹

Lead Ammonoacetate.—A solution of acetamide in liquid ammonia does not dissolve lead imide but converts it—slowly if the solution is only moderately concentrated, rapidly if very concentrated—into a pure white, amorphous product which settles well and is easily washed. After a few washings the precipitate begins to lose its pure white color and gradually takes on a color resembling that of lead imide, an indication, presumably, of the ammonolytic decomposition of the salt. The one specimen of this salt prepared was lost by the bursting of the container.

Silver Ammonobenzenesulfonate, $C_6H_5SO_2NHAg$, the Monammonate $C_6H_5SO_2NHAg \cdot NH_3$, and the Diammonate, $C_6H_5SO_2NHAg \cdot 2NH_3$.—Silver amide dissolves readily in a liquid ammonia solution of benzenesulfonamide to give a salt which separates in crystalline form when the solution, at proper concentration, is cooled in a bath of liquid ammonia. For analysis the salt was hydrolyzed by exposure to water vapor and dissolved in dilute sulfuric acid.

Preparation I.—The silver amide obtained from 0.85 g. of silver nitrate was dissolved in a solution of somewhat more than an equivalent amount of benzenesulfonamide and from the solution thus formed a crop of crystals (a) was obtained which was recrystallized once for analysis. From the mother liquor a second crop (b) was separated which was also once recrystallized.

Specimen (a) dried in vacuum at 130° weighed 0.5060 g. One-half gave 0.1327 g. AgCl, the other half gave 0.0193 g. N.

Specimen (b) dried in vacuum at -40° weighed 0.4435 g. Dried at 20° it weighed 0.4172 g. Dried at 200° it weighed 0.3914 g. One-half of the specimen dried at highest temperature gave 0.1031 g. AgCl, the other half gave 0.0111 g. N.

Preparation II.—The silver amide formed by the action of an equivalent quantity of potassium amide on one gram of silver nitrate was dissolved in a solution of somewhat more than one equivalent of benzenesulfonamide. The crop of crystals obtained was recrystallized once for analysis.

Dried in vacuum at -40° the specimen weighed 1.0689 g. After heating to 200° it weighed 1.0054 g. and after heating to 200° it weighed 0.9433 g. Two-tenths of

¹ J. Phys. Chem., 16, 690 (1912).

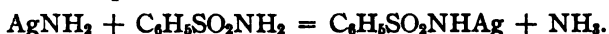
specimen, dried at 200°, gave 0.1624 g. AgI. In addition 0.0055 g. metallic silver, resulting from some reducing action in the container, was recovered, thus making the total silver present in the specimen 0.3795 g. Three-tenths of the specimen gave 0.0150 g. N.

Preparation III.—In order to avoid some slight decomposition of the salt, brought about by the high temperature necessary for the removal of the second molecule of ammonia, the specimen was dried for analysis at 20°. When the salt was dissolved in dilute sulfuric acid, preparatory to analysis, a perfectly clear, colorless solution resulted. In all respects, other than drying at 20° instead of at 200°, the conduct of this experiment was identical with that described under Preparation II.

The specimen dried in vacuum at -40° weighed 0.9602 g. Dried at 20° it weighed 0.9057 g. One-half of the specimen dried at 20° gave 0.2290 g. AgCl, the other half gave 0.0450 g. N.

	Calc. for C ₆ H ₅ SO ₂ NHAg.	Found.			
		Ia.	Ib.	II.	III.
Ag.....	40.8	39.5	39.8	40.2
N.....	5.3	7.6	5.7	5.3
Calc. for C ₆ H ₅ SO ₂ NHAg.NH ₃ .					
Ag.....	38.4	38.1
N (total).....	10.0	10.0
1 NH ₃	6.1	6.2	6.2
Calc. for C ₆ H ₅ SO ₂ NHAg.2NH ₃ .					
2 NH ₃	11.4	11.7	11.7
1 NH ₃	5.7	5.7

It is thus shown that silver amide dissolves in a liquid ammonia solution of benzenesulfonamide to form a silver salt of the acid amide in accordance with the equation,



Benzenesulfonamide silver separates from liquid ammonia solutions in the form of beautiful crystals containing two molecules of ammonia of crystallization. Of this ammonia one molecule is lost on warming to laboratory temperature, the other is expelled at temperatures around 200°. At the higher temperature, however, the salt undergoes slow decomposition, and there is a white sublimate, presumably of benzenesulfonamide, seen to collect in the upper, cooler portion of the specimen tube. The salt is extremely soluble in liquid ammonia at laboratory temperatures, much less soluble at low temperatures. Its solution in liquid ammonia shows the phenomenon of supersaturation in a striking degree. The salt is practically unaffected by exposure to light. It is hydrolyzed in the presence of water.

Preparation of Silver Ammonobenzenesulfonate by the Action of Benzenesulfonamide in Solution in Liquid Ammonia on Silver Oxide.—Silver oxide, which is insoluble in liquid ammonia, dissolves readily in

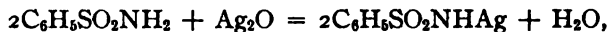
liquid ammonia solutions of benzenesulfonamide. A clear, colorless solution resulting from the treatment of 1 g. of silver oxide with slightly more than the equivalent quantity of the acid amide, after proper adjustment of the concentration, deposited a crop of beautiful needle-like crystals on cooling to the temperature of a liquid ammonia bath. After two recrystallizations the salt was treated first with water, then dissolved in dilute sulfuric acid for analysis.

Dried in vacuum at -40° the specimen weighed 1.2493 g. Dried at 20° it weighed 1.1851 g. One-half of the specimen dried at 20° gave 0.2977 g. AgCl, the other half gave 0.0471 g. N.

Calc. for $C_6H_5SO_2NHAg.NH_3$: Ag 38.4, N 10.0; found: 37.9 and 8.0.¹

Calc. for $C_6H_5SO_2NHAg.2NH_3$: 1 NH_3 5.7; found: 5.2.

The action of benzenesulfonamide in solution in liquid ammonia on silver oxide is, therefore, represented by the equation,



and the product obtained is identical with that formed by dissolving silver amide in benzenesulfonamide solution.

Thallous Ammonobenzenesulfonate, $C_6H_5SO_2NHTl$, the **Monammonate**, $C_6H_5SO_2NHTl.NH_3$, and the **Diammonate**, $C_6H_5SO_2NHTl.2NH_3$.—Thallium nitride dissolves readily in a solution of benzenesulfonamide to form a solution from which a well crystallized product may be obtained at low temperatures when the very strong tendency to form supersaturated solutions is overcome either by lucky chance or by some one of the devices known to be more or less effective to this end. After obtaining a crop of crystals the mother liquor was poured off and fresh solvent distilled back upon the crop of crystals in quantity sufficient to dissolve it when the temperature was allowed to rise. The dissolution of the crystals was carefully watched and before the last crystal remnant had disappeared, the solution was cooled to develop a new crop of crystals. The crystals grow beautifully when there are crystalline nuclei present in the solution, but in case the solid is once completely dissolved, then it becomes a difficult matter to initiate crystallization again. After three recrystallizations the preparation was submitted to the action of water vapor, then treated with liquid water, and finally dissolved in dilute sulfuric acid for analysis.

The specimen dried in vacuum at -70° weighed 1.4764 g. Dried at -40° its weight was, 1.4067 g.; at 20° , 1.3997 g.; and at 100° , 1.3422 g. One-half of the specimen dried at 100° gave 0.6090 g. TlI, the other half gave 0.0261 g. N.

Calc. for $C_6H_5SO_2NHTl$: Tl 56.6, N 3.9; found: 56.1 and 3.9.

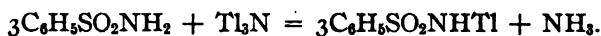
Calc. for $C_6H_5SO_2NHTl.NH_3$: 1 NH_3 4.5; found: 4.1 and 4.6.

Calc. for $C_6H_5SO_2NHTl.2NH_3$: 2 NH_3 8.6; found: 9.1.

These results show that benzenesulfonamide thallium is formed when

¹ Losses of ammonia were known to occur in making this determination.

thallous nitride is dissolved in a solution of benzenesulfonamide in liquid ammonia. The reaction is represented by the equation,



Thallium ammonobenzenesulfonate separates from concentrated solutions at low temperatures as well-formed crystals containing two molecules of ammonia of crystallization, which are lost stepwise as the temperature is allowed to rise. No attempts have been made to determine the vapor tension of these or of any of the other ammonates made during the course of this investigation. Solutions of the salt show, in a very conspicuous manner, the phenomenon of supersaturation. In a single instance crystallization was initiated at -40° , but no one of a considerable number of other attempts to bring about crystallization was successful until, by the use of liquid air, the operator was enabled to cool the solution to temperatures in the neighborhood of -70° . The very concentrated solutions become so viscous, when cooled to low temperatures, as to become practically solid without the least indication of crystallization. Once started, however, crystallization from a supersaturated solution proceeds in a manner beautiful to behold.

Thallous Ammono-*p*-toluenesulfonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl}$, and the Monammonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl.NH}_3$.—Thallous nitride dissolves readily in a liquid ammonia solution of *p*-toluenesulfonamide to form a clear, colorless solution from which a thallium salt of the acid amide may be crystallized by strongly cooling the properly concentrated solution.

Preparation I.—From a solution formed by dissolving the thallium nitride from 1.33 g. of thallium nitrate in a solution of somewhat more than one equivalent of *p*-toluenesulfonamide a crop of crystals was obtained which was recrystallized once, hydrolyzed and dissolved in dilute sulfuric acid for analysis.

Two-tenths of the specimen, dried in vacuum at 140° , weighed 0.4807 g., gave 0.0854 g. TlI. One-half of the specimen gave 0.0096 g. N.

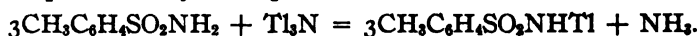
Preparation II.—From a solution formed by dissolving the thallium nitride from 1 g. of thallium nitrate in slightly more than one equivalent quantity of the acid amide, two crops of crystals, each of which was recrystallized once, were obtained and submitted to analysis with the following results:

Specimen (a) dried in vacuum at 20° weighed 0.2785 g. Heated to 118° , at which temperature the salt showed signs of melting, it weighed 0.2666 g. Four-tenths of the specimen dried at 118° gave 0.0935 g. TlI and 0.0040 g. N.

Specimen (b) dried in vacuum at -40° weighed 0.1619 g. Dried at 140° it weighed 0.1522 g. The whole specimen, dried at the latter temperature, gave 0.1363 g. TlI and 0.0066 g. N.

	Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl}$	Found.		
		I.	IIa.	IIb.
Tl.....	54.5	54.6	54.0	55.2
N.....	3.7	4.0	3.8	3.7
Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl.NH}_3$				
1 NH_3	4.3	4.3	6.0

p-Toluenesulfonamide thallium is, therefore, formed when thallium nitride is dissolved in a solution of the acid amide in accordance with the reaction represented by the equation,



The salt is very soluble in liquid ammonia at laboratory temperatures, much less so at lower temperatures. At low temperatures it separates from concentrated solutions with, probably,¹ two molecules of ammonia of crystallization, although this has not been proved of the specimens prepared. Dried at 20° the salt retains one molecule of ammonia. The ammonious salt melts at some temperature below 140°.

Cuprous Ammono-*p*-toluenesulfonate Diammonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu}_2.2\text{NH}_3$, and **Cupric Ammono-*p*-toluenesulfonate**, $(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH})_2\text{Cu}$.—Fitzgerald² found when a solution of cupric nitrate is treated with potassium amide that a precipitate is formed which, after being heated in vacuum to 160°, has the composition represented by the formula Cu_3N . Moreover the nitrogen set free during the reaction was determined and found to be evolved in an atomic ratio to copper always somewhat greater than one to three. It was, therefore, concluded that the reduction of the cupric to cuprous copper takes place during the reaction between the potassium amide and cupric nitrate and not during the heating of the precipitate. Proceeding on the assumption that Fitzgerald's precipitate is a cuprous compound, it was expected that it would dissolve in acid amide solutions to form a cuprous salt. However, when the supposedly pure cuprous imide was dissolved in *p*-toluenesulfonamide the resulting solution was found contaminated by the presence of more or less cupric salt.

Experiment I.—The precipitate formed by the action of potassium amide on 0.5 g. of tetrammonated cupric nitrate was treated with a liquid ammonia solution containing somewhat more than an equivalent quantity of toluenesulfonamide. On concentrating and cooling the resulting solution, a crystalline mass was formed which was made up of colorless crystals of a cuprous salt intermixed with needle-like crystals of a blue cupric compound. When crystallization took place from less concentrated solution a crop of bulky, interlacing, blue needles, containing no admixture of colorless crystals, was obtained. The mother liquor was poured from these crystals, which were then dissolved in pure solvent, distilled over from the

¹ Cf. Thallous benzenesulfonamide, p. 2268.

² THIS JOURNAL, 29, 656 (1907).

second leg of the reaction tube, and recrystallized. The salt was hydrolyzed, then dissolved in dilute hydrochloric acid and from the solution thus formed the copper was precipitated as sulfide by means of hydrogen sulfide.

Preparation I, dried in vacuum at 100° , weighed 0.0341 g. and gave 0.0068 g. Cu_2S .

On adjusting the concentration of the mother liquor from the above preparation and cooling to -40° a crop of colorless crystals, contaminated with a small quantity of the cupric salt, was obtained which, after one recrystallization, was dried and removed from the reaction tube for analysis.

Preparation II, dried in vacuum at -40° weighed 0.3061 g. Dried at 130° it weighed 0.2761 g. The whole specimen dried at 130° gave 0.0876 g. Cu_2S . One-half of the filtrate from the Cu_2S gave 0.0128 g. N.

Experiment II.—In a second experiment the precipitate, formed by the action of potassium amide on a solution containing 0.75 g. of ammonated cupric nitrate, was dissolved in somewhat more than an equivalent amount of *p*-toluenesulfonamide in solution in liquid ammonia. On cooling the solution a crop of bulky, blue crystals was obtained which was simply drained of mother liquor and submitted to analysis.

Preparation III weighed 0.0889 g. after heating in vacuum to 130° . The whole specimen gave 0.0188 g. Cu_2S and 0.0051 g. N.

On adjusting the concentration of the mother liquor from the preceding preparation and cooling in a bath of liquid ammonia a crop of colorless crystals, contaminated with a small quantity of cupric salt, separated from the solution. The product was recrystallized once for analysis.

Preparation IV, dried in vacuum at 20° , weighed 0.5036 g. Dried at 135° it weighed 0.4567 g. One-half of the specimen dried at 135° gave 0.0728 g. Cu_2S . The other half gave 0.0205 g. N.

	Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2\text{Cu}^1$	Found.	
		I.	III.
Cu.....	15.7	15.9	16.9
N.....	6.9	5.7
	Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu}, \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu} \cdot \text{NH}_3$	II.	IV.
Cu.....	27.2 25.4	25.3	25.5
N.....	6.0 11.2	9.3	9.0
	Calc. for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu} \cdot 2\text{NH}_3$		
Cu.....	23.8	22.8	23.2
N.....	15.7	16.4	15.8

It is obvious that both cupric and cuprous salts of *p*-toluenesulfonamide are formed when Fitzgerald's precipitate is dissolved in a solution

¹ The product analyzed may have been an equimolecular mixture of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu}$ and $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$ since it was unknown whether or not a reduction, similar to that discussed on p. 2274, had taken place at the temperature to which the preparation had been subjected.

of the acid amide, though it must be noted that the amount of cupric salt formed is relatively small. The presence of the cupric salt probably means, even in the face of the observations of Fitzgerald,¹ that the precipitate formed by the action of potassium amide on cupric nitrate contains a certain amount of cupric amide (or imide) which is completely converted into cuprous nitride only when the precipitate is heated.

From an inspection of the experimental data recorded above it is also obvious that a cuprous salt containing one molecule of ammonia cannot be obtained. Although the copper content of the preparations heated to 130–135° is in accord with that of a compound represented by the formula $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu}\cdot\text{NH}_3$, it will be noted that the amount of nitrogen present was about two per cent. too low. Elsewhere² in this paper it will be shown that the results obtained are best accounted for on the assumption that, under the influence of high temperature, ammonolytic decomposition accompanies the deammonation of the diammonated salt with the result that no sharply defined product is formed.

Cuprous Ammonobenzenesulfonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu}$, and the Diammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu}\cdot 2\text{NH}_3$.—A consideration of the difficulties encountered in effectively separating the cupric and cuprous salts of toluenesulfonamide led to successful attempts to reduce the cupric salt, which was present in the solutions described below, by treatment with metallic copper.

Preparation I.—The blue solution formed by dissolving the precipitate of cuprous imide from 2 g. of tetrammonated cupric nitrate in a liquid ammonia solution of 1.4 g. of benzenesulfonamide was allowed to lie in contact with a few pieces of copper foil until the color was discharged. The perfectly colorless solution resulting from this treatment was decanted from the bits of metallic copper, evaporated to high concentration and finally cooled in a bath of liquid ammonia for the purpose of obtaining a crop of crystals. However, the solution showed the phenomenon of supersaturation so tenaciously that the deposition of a crop of crystals could not be brought about until the tube was cooled almost to the freezing point of the solvent by means of a bath of alcohol cooled by liquid air. After crystals were once formed, however, the recrystallization of the salt could easily be carried on at the temperature of a liquid ammonia bath, provided complete solution of the compound was avoided. The crop of crystals first obtained was recrystallized twice for analysis. On heating the salt ammonia gas escaped without any apparent tendency to stepwise evolution.

The specimen dried in vacuum at -40° weighed 0.8319 g. After heating at 200° to 210° for more than an hour, at the end of which elapsed time ammonia was

¹ *Loc. cit.*

² Page 2273.

still escaping, though very slowly, the specimen weighed 0.7269 g. One-half of the specimen dried at the higher temperature gave 0.1390 g. Cu_2S , the other half gave 0.0269 g. N.

Preparation II.—The solution obtained by dissolving the cuprous imide from 1 g. of ammonated copper nitrate in 0.75 g. benzenesulfonamide in liquid ammonia solution was first decolorized, as described above, and then concentrated and cooled to a low temperature. After once overcoming the strong reluctance to crystallization the crop of crystals obtained was recrystallized once for analysis.

The specimen dried at -40° in vacuum weighed 0.6811 g. One-half gave 0.1059 g. Cu_2S , the other half gave 0.0572 g. N.

	Calc. for $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu}$.	Found. I.	Calc. for $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu} \cdot 2\text{NH}_3$.	Found.	
				I.	II.
Cu.....	29.0	28.8	25.1	25.1	24.8
N.....	6.4	7.4	16.6	16.9	16.8

The product of the action of benzenesulfonamide on cuprous imide is consequently a salt formed in accordance with the reaction represented by the equation,



Cuprous benzenesulfonamide separates from cold, concentrated solutions in the form of stout, colorless needles containing two molecules of ammonia of crystallization. It shows a large temperature coefficient of solubility, and is notable for its strong tendency to form supersaturated solutions. It is very susceptible to the action of atmospheric air, the least trace of which gaining entrance to the preparation tube causing the formation of a blue layer of the cupric salt on the surface of the solution. The ammonia of crystallization does not seem to come off stepwise, nor is all the ammonia removed by heating the preparation in vacuum to 200° for considerably over an hour. At elevated temperatures a quantity of colorless liquid, which solidifies on cooling, condenses in the upper portion of the container. Since it is scarcely possible that the salt itself sublimes, this liquid, which solidifies at lower temperature, must be free benzenesulfonamide resulting from the ammonolysis of the salt.

It is easy to understand the liberation of benzenesulfonamide and the observed fact that all the ammonia of crystallization cannot be removed from the salt, if it be assumed that ammonolysis takes place after the manner indicated by the equation,



and that the resulting cuprous amide—which is incapable of existence at the temperature¹ at which the ammonolysis is assumed to take place—is deammonated in accordance with the equation, $\text{CuNH}_2 = \text{CuN}_{1/2} + \frac{1}{2}\text{NH}_3$.

¹ Cf. THIS JOURNAL, 34, 1501 (1912).

Calculated in accordance with these equations the loss in weight of the specimen of diammonate, on heating, should have been 11.8%, whereas the observed loss was 12.6%, from which it may be concluded that the product analyzed was a mixture of an ammonious benzenesulfonamide, copper, free benzenesulfonamide and cuprous nitride, of the approximate composition represented by the formulas $(C_6H_5SO_2NHCu, C_6H_5SO_2NH_2, CuN_{1/2})$.

It is interesting to note that the decomposition which ammonate cuprous ammonobenzenesulfonate has thus been shown to undergo is entirely similar to the familiar reactions which take place when a certain hydrated salts, for example hydrated magnesium chloride, are heated.

Cupric Ammonobenzenesulfonate Tetrammonate, $(C_6H_5SO_2NH)_2Cu \cdot 4NH_3$, and the **Heptammonate**, $(C_6H_5SO_2NH)_2Cu \cdot 7NH_3$.—After the experiments described above¹ had shown that a cupric salt is formed simultaneously with the formation of a cuprous salt by the action of solution of an acid amide on Fitzgerald's precipitate, it was deemed desirable to attempt the preparation of a cupric salt by the action of a liquid ammonia solution of an acid amide on cupric oxide.

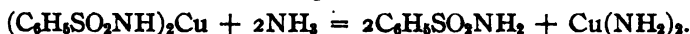
Preparation I.—Accordingly 0.3 g. of cupric oxide was treated with 10 times the equivalent quantity of benzenesulfonamide in solution in liquid ammonia. The immediate development of a blue color showed that the copper oxide was going into solution. After standing over night the solution had become intensely blue and the solution of the copper oxide was practically complete. Satisfactory recrystallization of the salt appeared impractical, because of the very bulky nature of the crop of crystals which separated when the solution was strongly cooled, such portions of the mother liquor as could be so removed were drained off and the salt submitted to the following described treatment:

Exposed in vacuum at -40° the salt dried to a blue, fibrous mass. As the temperature was raised ammonia was given off without showing the usual stepwise evolution. As the temperature approached 100° the blue color began to give way to a variegated green while at a somewhat higher temperature the solid salt changed to a semifluid, green mass and a white sublimate began to appear in the upper cooler portions of the tube. At 190° the preparation, which had changed in color from green to a dull yellow, was slowly giving off ammonia which, on examination, was found to contain a permanent gas, presumably nitrogen. The temperature at which evolution of nitrogen began was not determined. When the residue was treated with liquid ammonia a pale blue solution resulted which, on cooling, failed to give a bulky mass of blue crystals, but gave, instead, when very concentrated, a crop of colorless crystals intermixed with a small quantity of blue ones. Evaporation of the solvent at -40° left a light blue residue which, giving off ammonia continuously as the temperature was raised, melted at about 160° , and changed to a black, most unpromising mass as the temperature approached 270° . The salt, after this treatment, failed of complete solution when brought into contact with dilute hydrochloric acid, a mass of carbonaceous clots being left undissolved.

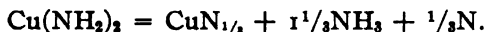
¹ Cf. p. 2270.

The results of the analysis, which are in rough agreement with the formula $(C_6H_5SO_2NH)_2Cu$ or $C_6H_5SO_2NHCu.C_6H_5SO_2NH_2$, are omitted here.

A plausible explanation of this reduction of the cupric to a cuprous salt may be given as follows: On heating the ammonated cupric salt, ammonolysis is assumed to take place in accordance with the equation,



Then, since Fitzgerald¹ has shown that cupric amide is incapable of existence, it follows that this product of the ammonolysis of the cupric salt must undergo reduction as represented by the equation,



On now treating the residual mixture with liquid ammonia, the cuprous nitride dissolves in the excess of acid amide to form the cuprous salt of benzenesulfonamide.²

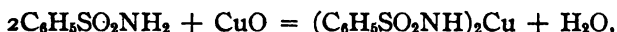
Preparation II.—While working with the solution of another preparation, obtained in the manner described above, it was found that, by concentrating the solution at the temperature of the laboratory, the salt could be crystallized in the form of short, thick, very soluble prisms from which the mother liquor could be fairly satisfactorily drained. A crop of crystals so obtained was dissolved in dilute hydrochloric acid for analysis.

The specimen dried in vacuum at -40° weighed 0.5047 g. After heating to 20° it weighed 0.4524 g. Three-tenths of the specimen dried at 20° gave 0.0236 g. Cu_2S , another three-tenths gave 0.0266 g. N.

Calc. for $(C_6H_5SO_2NH)_2Cu.4NH_3$: Cu 14.3, N 18.9; found (II): 15.0 and 19.6.

Calc. for $(C_6H_5SO_2NH)_2Cu.7NH_3$: $3NH_3$ 10.3; found: 10.4.

It, therefore, appears that cupric oxide dissolves in liquid ammonia solutions of benzenesulfonamide to form a cupric salt in accordance with the equation



and that this salt separates from solution with seven molecules of ammonia, three of which it loses in vacuum at 20° . On heating to higher temperatures the cupric salt is converted into a mixture of cuprous ammonobenzenesulfonate and the free acid amide.

Metallic Salts of the Acid Ammono Esters.

The acid amides are to be looked upon as dibasic ammono acids, and in accordance with this view Franklin and Stafford³ found benzamide and benzenesulfonamide, for example, to react with potassium amide in liquid ammonia solutions to form acid and normal salts of the respective formulas C_6H_5CONHK , $C_6H_5SO_2NHK$, $C_6H_5CONK_2$ and $C_6H_5SO_2NK_2$.

¹ *Loc. cit.*

² It may be noted that the reduction of the cupric salt may be represented as taking place in accordance with the equation, $(C_6H_5SO_2NH)_2Cu.4NH_3 = C_6H_5SO_2NHCu + C_6H_5SO_2NH_2 + 3\frac{1}{2}NH_3 + \frac{1}{2}N$.

³ *Am. Chem. J.*, 27, 83 (1902).

Now if the acid amides are in reality the acids of an ammonia system of acids, bases and salts,¹ then it follows that their alkyl and aryl derivatives must be looked upon as ammono esters, and since there are in the acid amides two replaceable hydrogen atoms, either one or both of which may be replaced by hydrocarbon radicals, then one is led to the conclusion that such derivatives of the acid amides will show the properties, respectively, of acid ammono esters and neutral ammono esters. It was to test the question as to whether such acid esters behave as acids in solution in liquid ammonia that the experiments described below were undertaken.

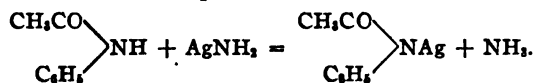
Silver Phenyl Ammonoacetate, $\text{CH}_3\text{CONAgC}_6\text{H}_5$, and the Monammonate, $\text{CH}_3\text{CONAgC}_6\text{H}_5\cdot\text{NH}_3$.—A compound which is at the same time an ammono salt and an ammono ester. Pure silver amide, prepared from 1 g. of silver nitrate in a manner which has been elsewhere described, was found to dissolve readily enough in a liquid ammonia solution of 1 g. of acetanilide, especially when the solution was concentrated. The salt formed is very soluble in liquid ammonia and could be brought to crystallization only by exposing the concentrated solution to a temperature of -70° or below. The crystals separated as a very bulky mass which retained much mother liquor, so the one recrystallization to which the specimen was submitted cannot have accomplished very much toward the purification of the salt. Preparatory to analysis the compound was first hydrolyzed, then dissolved in dilute sulfuric acid.

Dried in vacuum at 20° the specimen weighed 0.3323 g. After heating to 100° it weighed 0.3100 g. The whole specimen dried at 100° gave 0.1892 g. AgCl . N was lost.

Calc. for $\text{CH}_3\text{CONAgC}_6\text{H}_5$: Ag 44.7; found: 45.9.

Calc. for $\text{CH}_3\text{CONAgC}_6\text{H}_5\cdot\text{NH}_3$: 1 NH_3 6.6; found: 6.7.

The formation of a silver salt of acetanilide by the action of the acid ester in solution in liquid ammonia on silver amide is thus shown to take place in accordance with the equation



When cooled to a low temperature the very soluble salt separates from concentrated solutions as a bulky, crystalline mass containing ammonia of crystallization. One molecule of ammonia is retained at 20° to be given off when the salt is heated to 100° .

Thallous Phenyl Ammonoacetate, $\text{CH}_3\text{CONTIC}_6\text{H}_5$.—When the precipitate of thallium nitride prepared from 1.3 g. of thallium nitrate was allowed to lie in contact with a liquid ammonia solution of somewhat more than the equivalent amount of acetanilide, the black nitride was

¹ Cf. *Am. Chem. J.*, 47, 285 (1912).

gradually converted into a gray, granular mass which is but slightly soluble in liquid ammonia.

Preparation Ia.—By repeatedly extracting this product with liquid ammonia a good crop of colorless crystals was collected in the second arm of the reaction tube. Preparatory to analysis the specimen was first treated with water, then dissolved in dilute sulfuric acid.

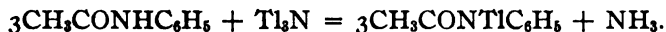
Dried in vacuum at 20° the specimen weighed 0.7796 g. After heating to 100° it weighed 0.7778 g. One-half of the specimen gave 0.3773 g. TlI, the other half gave 0.0151 g. N.

Preparation Ib.—The gray residue, from which the above specimen was extracted, was washed to remove the excess of acetanilide present and submitted to analysis with the following results:

Dried in vacuum at 20° the specimen weighed 0.5541 g. Dried at 100° it weighed 0.5533 g. One-half of the specimen gave 0.2685 g. TlI, the other half gave 0.0108 g. N.

Calc. for $\text{CH}_3\text{CONTC}_6\text{H}_5$: Tl 60.4, N 4.1; found: (Ia) 59.8 and 3.9; (Ib) 59.8 and 3.9.

From the results of the above described experiments it follows that thallium nitride is converted into a thallium salt of acid phenyl ammonoacetate, when the nitride is allowed to lie in contact with a solution of acetanilide, in accordance with the equation



The salt is only slightly soluble in liquid ammonia but may be obtained in the form of well developed, colorless crystals by shaking the gray reaction product, mentioned above, in contact with liquid ammonia until a saturated solution is obtained, pouring the solution from the residue, and evaporating away the greater portion of the solvent. It separates from solution without ammonia of crystallization.

Potassium Benzyl Ammonoacetate Monammonate, $\text{CH}_3\text{CONKCH}_2\text{-C}_6\text{H}_5\cdot\text{NH}_3$.—(Prepared by Mr. W. R. Weaver.¹) Liquid ammonia solutions of benzylacetamide² and potassium amide were brought together with the resultant formation of a bright red solution from which, after bringing to a sufficiently high concentration and cooling to a low temperature, an abundant crop of pink crystals was obtained. After draining off the mother liquor and washing a few times with small quantities of liquid ammonia, the preparation was treated with water and then dissolved in dilute sulfuric acid for analysis.

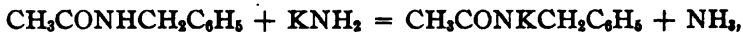
Dried in vacuum at 20° the specimen weighed 0.1338 g. One-half gave 0.0282 g. K_2SO_4 , the other half gave 0.0084 g. N.

Calc. for $\text{CH}_3\text{CONKCH}_2\text{C}_6\text{H}_5\cdot\text{NH}_3$: K 19.1, N 13.7; found: 19.1 and 12.6.

¹ From a thesis submitted to the Department of Chemistry of the Leland Stanford Junior University in partial fulfillment of the requirements for the degree of Master of Arts.

² This compound was made by heating together benzylamine and glacial acetic acid and purifying the reaction product by fractional distillation. Benzylacetamide is very easily soluble in liquid ammonia.

Benzylacetamide, therefore, reacts with potassium amide in liquid ammonia solution in accordance with the equation,



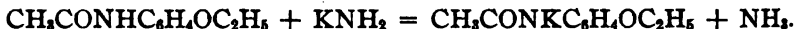
to form a salt which retains one molecule of ammonia of crystallization when dried in vacuum at 20°. The salt is very soluble in liquid ammonia and separates from concentrated, cold solutions beautifully crystallized.

Potassium *p*-Phenetol Ammonoacetate, $\text{CH}_3\text{CONKC}_6\text{H}_4\text{OC}_2\text{H}_5$.—(Prepared by W. R. Weaver.) Phenetolacetamide is very soluble in liquid ammonia. Solutions of approximately equivalent quantities of the acid ammono ester and potassium amide, when brought together, gave a solution from which a crop of crystals could be obtained only at very high concentration and low temperature. The mother liquor, very limited in quantity, was drained from the crystals and they were washed to some extent by first properly inclining the reaction tube so that the liquid would drain off, and then condensing small quantities of ammonia upon the crystals by the application of a swab of cotton, saturated with liquid ammonia, to the exterior of the tube. The purification of the preparation was not considered very satisfactory. For analysis the salt was dissolved in dilute sulfuric acid.

One-half of the specimen, which dried in vacuum at 20° weighed 0.2024 g., gave 0.0422 g. K_2SO_4 . The remaining half gave 0.0060 g. N.

Calc. for $\text{CH}_3\text{CONKC}_6\text{H}_4\text{OC}_2\text{H}_5$: K 17.9, N 6.4; found: 18.1 and 5.9.

These analytical results show in a fairly satisfactory manner that potassium phenetol ammonoacetate is formed by the action of potassium amide on phenetolacetamide in accordance with the equation



The salt, which is extremely soluble in liquid ammonia, separates well crystallized from very concentrated, cold solutions, and retains no ammonia when dried in vacuum at 20°.

Summary.

In this investigation it has been shown, in the first place, that the amides, imides and nitriles of certain heavy metals dissolve in liquid ammonia solutions of acid amides to form well crystallized metallic derivatives of the acid amides. The compounds obtained are to be looked upon as salts of an ammonia system of acids, bases and salts which are formed by the action of ammono acids on ammono bases in liquid ammonia solutions.

In the second place it has been shown that such compounds as acetanilide and benzylacetamide are to be looked upon as acid ammono esters which, in liquid ammonia solutions, react with ammono bases, just as the acid amides do, to form ammono salts.

The following salts, for the most part beautifully crystallized, have been prepared:

1. Diammonated silver ammonoacetate, $\text{CH}_3\text{CONHAg} \cdot 2\text{NH}_3$.
2. Thallous ammonoacetate, CH_3CONHTl and the diammonate, $\text{CH}_3\text{CONHTl} \cdot 2\text{NH}_3$.
3. Lead ammonoacetate.
4. Silver ammonobenzenesulfonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHAg}$, the monammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHAg} \cdot \text{NH}_3$ and the diammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHAg} \cdot 2\text{NH}_3$.
5. Thallous ammonobenzenesulfonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHTl}$, the monammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHTl} \cdot \text{NH}_3$ and the diammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHTl} \cdot 2\text{NH}_3$.
6. Thallous ammono-*p*-toluenesulfonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl}$ and the monammonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHTl} \cdot \text{NH}_3$.
7. Diammonated cuprous ammono-*p*-toluenesulfonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCu} \cdot 2\text{NH}_3$.
8. Cupric ammono-*p*-toluenesulfonate, $(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH})_2\text{Cu}$.
9. Cuprous ammonobenzenesulfonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu}$ and the diammonate, $\text{C}_6\text{H}_5\text{SO}_2\text{NHCu} \cdot 2\text{NH}_3$.
10. Cupric ammonobenzenesulfonate tetrammonate, $(\text{C}_6\text{H}_5\text{SO}_2\text{NH})_2\text{Cu} \cdot 4\text{NH}_3$ and the heptammonate, $(\text{C}_6\text{H}_5\text{SO}_2\text{NH})_2\text{Cu} \cdot 7\text{NH}_3$.
11. Silver phenylammonoacetate, $\text{CH}_3\text{CONAgC}_6\text{H}_5$ and the monammonate, $\text{CH}_3\text{CONAgC}_6\text{H}_5 \cdot \text{NH}_3$.
12. Thallous phenylammonoacetate, $\text{CH}_3\text{CONTIC}_6\text{H}_5$.
13. Potassium benzyl ammonoacetate monammonate, $\text{CH}_3\text{CONKCH}_2\text{C}_6\text{H}_5 \cdot \text{NH}_3$.
14. Potassium *p*-phenetol ammonoacetate, $\text{CH}_3\text{CONKC}_6\text{H}_4\text{OC}_2\text{H}_5$.

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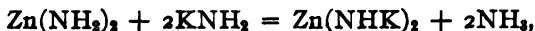
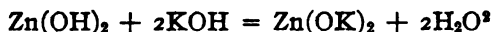
POTASSIUM AMMONOBARATE, AMMONOSTRONTIATE AND AMMONOCALCIATE.

BY EDWARD C. FRANKLIN.

Received July 8, 1915.

Introduction.

Investigations¹ conducted in this laboratory have shown that a reaction similar to that which accompanies the solution of the hydroxide of zinc in aqueous potassium hydroxide takes place when the amide of zinc is treated with a liquid ammonia solution of potassium amide. These strikingly similar reactions proceed in accordance with the equations,



¹ Fitzgerald, *THIS JOURNAL*, 29, 660 (1907), and Franklin, *Ibid.*, 29, 1275 (1907).

² As a matter of fact this equation, which is frequently written to represent the action of potassium hydroxide on zinc hydroxide, seems never to have been experimentally demonstrated (cf. Comey and Jackson, *Am. Chem. J.*, 11, 145 (1894)).

which represent, respectively, the formation of an aquozincate and an ammonozincate of potassium, the one a salt of the water system of acids, bases and salts, the other, a salt of the ammonia system.

Following the successful preparation of the ammonozincate and the ammonoplumbite¹ of potassium, which are the analogs of known aquo-compounds, other metallic amides (imides and nitrides) were studied with respect to their behavior toward liquid ammonia solutions of potassium amide, with the result—perhaps contrary to what was to have been expected in view of the fact that only a limited number of metallic hydroxides are known to react with potassium hydroxide—that the capacity of forming salts similar to potassium ammonozincate came to be recognized as a property possessed by many, perhaps a majority, of the commoner metals. In the course of these investigations it has been found that potassium amide reacts with cadmium amide to form an ammonocadmiate of potassium,² with nickel amide to form an ammononickelate,¹ with silver amide to form an ammonoargentate,³ with cuprous imide to form an ammonocuprite,⁴ with thallos nitride to form an ammonothallite⁵ and even with the amide of the strongly electropositive magnesium to form an ammonomagnesate of potassium.⁶ The isolation of compounds such as these, and especially the preparation of an ammonomagnesate of potassium as a compound of sharply definite composition, suggested the possibility that the amides of the more positive metals, barium, strontium and calcium, might be capable of reacting with potassium amide to form similar ammono salts.

Before passing to a description of the experimental part of this research it is interesting to note that—in contrast with the difficulties encountered by other investigators in their efforts to prepare satisfactory specimens⁷ of the aquozincates and aquoplumbites and even of the aquo-aluminates—the ammono salts mentioned above are easily prepared, and for the most part have been obtained beautifully crystallized and of sharply definite composition. The formation of amorphous products

¹ *J. Phys. Chem.*, **15**, 511 (1911).

² *Ibid.*, October, 1915.

³ *THIS JOURNAL*, **37**, 854 (1915).

⁴ *Ibid.*, **34**, 1501 (1912).

⁵ *J. Phys. Chem.*, **16**, 682 (1912).

⁶ *THIS JOURNAL*, **35**, 1455 (1913). An ammonostannate (*Ibid.*, **29**, 1693 (1907)), and an ammonotitanate of potassium (*Ibid.*, **34**, 1497 (1912)), analogous to the familiar aquostannate and aquotitanate, have also been prepared in this laboratory, but since stannic and titanic hydroxides are distinct acids and scarcely show amphoteric properties, their ammono salts are not of very particular interest in the present connection.

⁷ Prescott, *THIS JOURNAL*, **2**, 27 (1880), Comey and Jackson, *Am. Chem. J.*, **11**, 145 (1894), Allen and Rogers, *Ibid.*, **24**, 304 (1901), Hantzsch, *Z. anorg. Chem.*, **30**, 289 (1902).

interferes with the isolation of pure aquo salts. Nothing of the kind appears to stand in the way of the preparation of the ammono salts.

Experimental.

Since the special methods which have been developed in this laboratory for the manipulation of liquid ammonia solutions have been described elsewhere,¹ it is unnecessary to go into detail concerning them here.

Potassium Ammonobarate, $\text{BaNK}_2\cdot 2\text{NH}_3$, $\text{Ba}(\text{NH}_2)_2\cdot \text{KNH}_2$ or $[\text{Ba}(\text{NH}_2)_3]\text{K}$.—When a barium salt and an excess of potassium amide are brought together in liquid ammonia solution a white, insoluble precipitate is formed which has been shown to have the composition represented by the above formulas. Preparatory to analysis, the pure, dry² salt was hydrolyzed by the action of water vapor, then treated with liquid water and finally dissolved in dilute hydrochloric acid. From an aliquot portion of the acid solution the barium was removed and weighed as sulfate. The filtrate from barium sulfate was evaporated to dryness and the residue ignited and weighed as potassium sulfate. From another portion of the solution ammonia was removed by distillation with excess of potassium hydroxide and determined by titration after the usual manner with standard acid.

Preparation I.—Into a large excess of potassium amide was run a solution of 1 g. of barium nitrate which had been previously dried by gentle ignition. The resulting precipitate was washed many times, by the process of decantation described elsewhere, in order to be sure of removing all the potassium nitrate formed in the reaction, together with the excess of potassium amide used.

Dried in vacuum at 20° the preparation weighed 1.1525 g. One-half gave 0.6040 g. BaSO_4 . One-fifth gave 0.0515 g. NH_3 . One-fifth of the filtrate from BaSO_4 gave 0.0916 g. K_2SO_4 .

Preparation II.—After pouring barium nitrate solution into a solution containing a large excess of potassium amide, the reaction tube with its contents—subjected to occasional shaking—was allowed to stand several days with the object in view of ascertaining whether a compound richer in potassium than Preparation I might be obtained. After thorough washing the precipitate was dried in vacuum, first at -40° and then at 20° . By this treatment the preparation lost only 0.0012 g., thus showing that at the lower temperature the compound retains but two molecules of ammonia.

Dried at 20° the specimen weighed 1.2873 g. One-fourth gave 0.3371 g. BaSO_4 . Another fourth gave 0.0608 g. N. The filtrate from BaSO_4 gave 0.1244 g. K_2SO_4 .

¹ THIS JOURNAL, 27, 820 (1905); 29, 656 and 1693 (1907); 35, 1455 (1913); J. Phys. Chem., 15, 509 (1911); 16, 682 (1912).

² Free from uncombined ammonia.

Preparation III.—This experiment was a duplicate of the preceding, excepting that instead of pouring the barium nitrate into an excess of potassium amide the order of mixing the solutions was reversed.

Dried at 20° in vacuum the specimen weighed 1.2900 g. One-fourth gave 0.3366 g. BaSO₄ and 0.1260 g. K₂SO₄. One-fourth gave 0.0602 g. N.

Preparation IV.—This and the succeeding preparation were made by the action of potassium amide on the very soluble barium sulfocyanate. A solution of 0.55 g. of the salt, which had been dried for several weeks in vacuum over sulfuric acid, was added to an excess of potassium amide in liquid ammonia solution. The precipitate formed was thoroughly washed preparatory to analysis.

The specimen dried at 20° in vacuum weighed 0.5480 g. and gave 0.5506 g. BaSO₄. One-half of the filtrate from BaSO₄ gave 0.1149 g. K₂SO₄; one-fifth gave 0.0204 g. N.

Preparation V.—In this experiment an excess of potassium amide was added to a solution of 0.61 g. barium sulfocyanate. The precipitate was thoroughly washed.

Dried in vacuum at 100° the specimen weighed 0.4404 g. and gave 0.4432 g. BaSO₄. One-half of the filtrate from BaSO₄ gave 0.0923 g. K₂SO₄; the other half gave 0.0415 g. N.

	Calc. for BaNK.2NH ₃ .	Found.				
		I.	II.	III.	IV. ¹	V. ¹
Ba.....	61.2	61.6	61.6	61.3	59.2	59.2
N.....	18.7	18.4	18.9	18.7	18.6	18.8
K.....	17.4	17.8	17.4	17.5	18.8	18.6

Potassium ammonobarate, which is formed in accordance with the equation



when barium nitrate in solution in liquid ammonia is poured into an excess of a solution of potassium amide, is obtained as an amorphous or microcrystalline precipitate of the composition represented by the formula BaNK.2NH₃. Temperatures up to 100° have no effect on the compound. It is insoluble in liquid ammonia, but is decomposed and dissolved in liquid ammonia solutions of ammonium nitrate. It is hydrolyzed vigorously in contact with water into potassium hydroxide, barium hydroxide and ammonia.

Barium Amide, Ba(NH₂)₂.—Although barium amide has been previously prepared² it was thought desirable in this connection to show that it may be obtained by the action of potassium amide on barium salts in liquid ammonia solution. Accordingly, in one experiment potassium

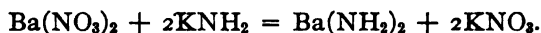
¹ The barium thiocyanate used in making these preparations was supposed, at the time it was used, to be dry. It was subsequently found to contain water. The high content of potassium and the low results for barium are, therefore, due to the presence of potassium hydroxide formed by the action of the water on potassium amide.

² Mentrel, *Bull. soc. chim.* (France), [3] 29, 497 (1903); Guntz et Mentrel, *Ibid.*, [3] 29, 578 (1903).

amide was run into a large excess of a solution of barium nitrate, in another, barium nitrate was added to two equivalents of potassium amide, in a third, equivalent quantities of barium sulfocyanate and potassium amide were mixed, and in a fourth, a dilute solution of potassium amide was run very slowly—with constant shaking—into a large excess of barium sulfocyanate solution in the hope that the inclusion of any potassium ammonobarate in the precipitate might thus be avoided. The realization of a pure compound, however, was defeated by the presence of water in the barium thiocyanate used, which, of course, resulted in the contamination of the precipitate with a small quantity of potassium hydroxide. Since barium amide is a compound already known, the inclusion of the analytical data here is unnecessary. Following are the results obtained:

	Calc. for $\text{Ba}(\text{NH}_2)_2$	Found.			
		I.	II.	III.	IV.
Ba.....	81.0	79.7	79.4	80.6	80.5
N.....	16.6	15.7	16.0	15.3	15.6
K.....	0.0	1.5

These results show that barium amide is formed by the action of potassium amide on a salt of barium in solution in liquid ammonia, but obviously the preparation of a pure compound in this manner is a matter of considerable difficulty. The action is represented by the equation



Barium amide was obtained as a white precipitate insoluble in liquid ammonia, but readily soluble in a solution of ammonium nitrate.

Potassium Ammonostrontiate, $\text{SrNK}_2\cdot 2\text{NH}_3$, $\text{Sr}(\text{NH}_2)_2\cdot \text{KNH}_2$ or $[\text{Sr}(\text{NH}_2)_2]\text{K}$.—Excepting that a soluble strontium salt was substituted for the barium salt, the procedure followed for the preparation of potassium ammonostrontiate was the same as that described above for obtaining potassium ammonobarate. The strontium was determined as carbonate and the potassium as chloride.

Preparation I.—One gram of strontium nitrate, dried by gentle ignition, was dissolved in liquid ammonia and added to a solution of four equivalents of potassium amide. A bulky, amorphous precipitate resulted. Due to a leaky stopcock the solvent evaporated away while the preparation tube stood over night, leaving the precipitate in the form of lumpy masses which were not broken up by the washing to which they were subjected. There was, therefore, some doubt as to the efficiency of the washing.

The specimen dried in vacuum at 20° weighed 0.9725 g. One-fourth gave 0.1976 g. SrCO_3 , and 0.1114 g. KCl . One-fifth gave 0.0439 g. N.

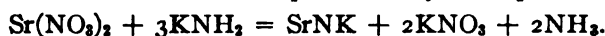
Preparation II.—This specimen was made by running a solution of 1 g. of strontium nitrate into a solution containing approximately three equiva-

lents of potassium amide. The precipitate was thoroughly washed preparatory to analysis.

Dried at 100° in vacuum the specimen weighed 0.7816 g. One-half gave 0.3329 g. SrCO_3 and 0.1680 g. KCl . One-eighth gave 0.0233 g. N.

	Calc. for $\text{SrNK} \cdot 2\text{NH}_3$	Found.	
		I.	II.
Sr.....	50.1	48.3	50.4
N.....	24.0	22.6	23.8
K.....	22.4	24.0	22.6

Although obtained in the form of a bulky, amorphous precipitate there can be no doubt of the formation of an ammonostrontiate of potassium as the result of the action of potassium amide in excess on solutions of strontium salts. The reaction is represented by the equation



The salt is insoluble in liquid ammonia but dissolves in solutions of ammonium nitrate to form the nitrates of strontium and potassium. It is hydrolyzed vigorously by water into strontium hydroxide, potassium hydroxide and ammonia.

Potassium Ammonocalciate, $\text{CaNK} \cdot 2\text{NH}_3$, $\text{Ca}(\text{NH}_2)_2 \cdot \text{KNH}_2$ or $[\text{Ca}(\text{NH}_2)_2]\text{K}$.—This salt has been prepared by the action of potassium amide on metallic calcium and by adding calcium thiocyanate to an excess of a solution of potassium amide. Preparatory to analysis the salt was hydrolyzed by water vapor and dissolved in dilute hydrochloric acid. The calcium was precipitated as oxalate and weighed as oxide. Potassium was weighed as chloride and ammonia was determined by the usual volumetric method.

Preparation I.—Into the two legs of the familiar reaction tube were introduced, respectively, 0.2 g. metallic calcium and 0.4 g. metallic potassium, the latter together with a small quantity of platinum black. As soon as the potassium had been converted into potassium amide, the solution of this ammono base was poured into the leg containing the metallic calcium. The blue color of the calcium solution disappeared in the course of an hour, leaving a white, amorphous precipitate, which, after thorough washing, was submitted to analysis.

The specimen dried in vacuum at 80° weighed 0.5707 g. One-half gave 0.1221 g. CaO and 0.1817 g. KCl . One-fourth gave 0.0457 g. N.

Preparation II.—This experiment was practically a duplicate of the preceding.

Dried in vacuum at 100° the precipitate weighed 0.6285 g. One-fourth gave 0.0694 g. CaO and 0.0944 g. KCl . Another fourth gave 0.0510 g. N.

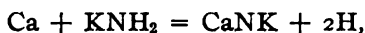
Preparation III.—Six-tenths of a gram of calcium sulfocyanate, which had been dried by heating to 100° in vacuum for several hours, was dissolved in liquid ammonia and added to an excess of potassium amide solu-

tion. The pulverulent precipitate formed was washed many times by the decantation method and dried at 110° for analysis.

The specimen weighed 0.4754 g. Six-tenths gave 0.1258 g. CaO and 0.1735 g. KCl. Two-tenths gave 0.0300 g. N.

	Calc. for CaNK. 2NH_3 .	Found.		
		I.	II.	III.
Ca.....	31.5	30.6	31.5	31.5
N.....	33.1	32.0	32.5	31.6
K.....	30.8	33.4	31.4	31.8

Although the analytical results are distinctly unsatisfactory there can scarcely be a doubt of the formation of a potassium ammonocalciate of the formula CaNK. 2NH_3 , first, by the action of potassium amide on metallic calcium as represented by the equation



and second, by the action of excess of potassium amide on a solution of a salt of calcium as represented by the equation



The salt is apparently amorphous, but settles well to a fairly dense, granular precipitate which is easily washed. It dissolves readily in liquid ammonia solution of ammonium nitrate. In contact with water it is energetically hydrolyzed to calcium hydroxide, potassium hydroxide and ammonia.

Summary.

It has been shown in this paper that just as the amides of zinc and magnesium are acted upon by potassium amide in liquid ammonia solution to form an ammonozincate and an ammonomagnesate of potassium, so the amides of barium, strontium and calcium, when submitted to the action of solutions of the ammonio base, are similarly converted into an ammonobarate, an ammonostrontiate and an ammonio calciate of potassium, respectively.

General formulas for the compounds obtained are the following: $\text{MeNK} \cdot 2\text{NH}_3$, $\text{NH}_2\text{MeNHK} \cdot \text{NH}_3$, $\text{Me}(\text{NH}_2)_2 \cdot \text{KNH}_2$ or following Werner, $[\text{Me}(\text{NH}_2)_3]\text{K}$.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 23.]

LIQUID JUNCTION POTENTIALS.

BY DUNCAN A. MACINNES.

Received June 2, 1915.

A concentration cell with transference, consisting of two similar reversible electrodes in contact with two differently concentrated solutions

of the same salt, will give an electromotive force which is the algebraic sum of three potentials: the voltages at the two electrodes and the potential at the junction of the solutions. Since, for many theoretical purposes, the potential at the electrodes alone is desired, many attempts have been made to evaluate the potential at the liquid junction. Formulas have been proposed for this purpose by Nernst,¹ Planck,² Henderson,³ Cumming,⁴ and others. Bjerrum,⁵ Cumming⁶ and Sackur⁷ have studied the effect of interposing strong salt solutions on the electromotive force of the cell with a view of eliminating the effect of the liquid junction.

It has been usual to test the correctness of the value of the potential assigned to the junction, or the efficacy of the artifice employed in eliminating it, by seeing whether the resulting voltage at the electrodes can be calculated from the Nernst equation in its kinetic form:

$$E = \frac{RT}{F} \ln \frac{C_i}{C_i'} \quad (1)$$

where C_i and C_i' are the concentrations of the ions in the two solutions as calculated from conductance measurements. (E = electromotive force, R the gas constant, T the absolute temperature, and F the faraday, respectively.) As the substitution of values of ion concentrations determined from conductance measurements into the partially thermodynamic equations

$$E = \frac{2n_c RT}{F} \ln \frac{C_i}{C_i'} \quad \text{and} \quad E = \frac{2RT}{F} \ln \frac{C_i}{C_i'}$$

for cells with and without transference, has been shown⁸ to give higher values of the electromotive force than are found by direct measurement; it is altogether probable that Equation 1 will also give too high values for the voltages at the electrodes of a cell with diffusion. For this reason the potentials of the liquid junctions, adopted on the assumption that Equation 1 gives the correct values for the voltage at the electrodes, will probably be too small. It is also very evident that the early workers in this field did not require very close accord of their predicted values of the electromotive force with those found by experiment in order to conclude that their theoretical premises were established. It therefore

¹ *Z. physik. Chem.*, 2, 613 (1888).

² *Wied. Ann.*, 40, 561 (1890).

³ *Z. physik. Chem.*, 59, 118 (1906), and 63, 325 (1908).

⁴ *Trans. Faraday Soc.*, 8, 86 (1912).

⁵ *Z. physik. Chem.*, 53, 428 (1905).

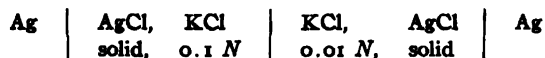
⁶ *Trans. Faraday Soc.*, 2, 213 (1907).

⁷ *Z. physik. Chem.*, 48, 129 (1904).

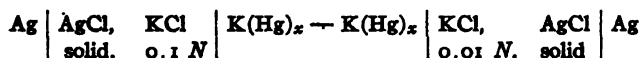
⁸ See, for instance, Jahn, *Z. physik. Chem.*, 33, 545 (1900); Tolman and Ferguson, *This Journal*, 34, 232 (1912); MacInnes and Parker, *Ibid.*, 37, 1445 (1915).

seems desirable to investigate the subject of the liquid junction connecting two solutions of the same salt with a view to finding an expression, involving the fewest possible assumptions, for its electromotive force.

If we allow the cell



to operate reversibly until one faraday has passed through it, one equivalent of chloride ions will enter the dilute solution and a similar amount will be electrolyzed out of the more concentrated solution. The current will be carried across the liquid junction by the movement of n_c equivalents of potassium ion in direction of the current and by the migration of $(1 - n_c)$ equivalents of chloride ion in the reverse direction, n_c being the transference number of the cation. The total effect of the passage of the faraday of electricity will be the transference of n_c equivalents of salt from the more concentrated to the dilute solution. Now the osmotic work at the liquid junction will depend on the algebraic sum of the number of equivalents of ion that have been carried across it from the concentrated to the dilute solution, in this case equal to $n_c - (1 - n_c) = 2n_c - 1$. This, of course, involves the assumption that the osmotic work involved in the transferring of a gram equivalent positive ion from a dilute to a concentrated solution is the same as the work necessary for the transfer of a corresponding amount of negative ion. Now in order to obtain the electrical work, and with it the voltage, by which this osmotic work is accomplished, let us consider the cell without transference:



The operation of this cell consists in the formation of one equivalent each of potassium ion and chloride ion in the dilute solution during the passage of one faraday of electricity, and at the same time the removal of one equivalent of each ion from the more concentrated solution. The electrical energy accompanying the transfer of the two equivalents of ion from one solution to the other will be the electromotive force of the cell, E , multiplied by the value of the faraday, F .

The electromotive force of the liquid junction, E_L , can now be obtained by the simple proportion:

$$EF : E_L F = 2 : 2n_c - 1 \quad \text{or} \quad E_L = E(2n_c - 1)/2 \quad (2)$$

Since our problem is that of apportioning the total voltage of a cell with transference between the electrode potentials and the liquid junction, we may replace the E , M. F. of the cell without transference, E , by that of the cell with transference, E_b , with the aid of the relation: $E_b = E n_c$.¹ This formula, the derivation of which involves only the two

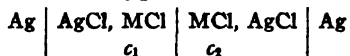
¹ See MacInnes and Parker, *THIS JOURNAL*, 37, 1445 (1915).

laws of thermodynamics, has been tested experimentally for cells of both types involving solutions of KCl and HCl. Making the substitution, (2) becomes

$$E_c = (E_i/2n_c)(2n_c - 1) = E_i(1 - 1/2n_c), \quad (3)$$

an equation which contains no assumption regarding the concentration of the ions of the two solutions.

A direct test of this simple equation is, of course, not possible, but an indirect one is afforded by the following considerations: The electrode potential, *i. e.*, the E. M. F. of the cell minus the potential of the liquid junction, for cells of the type



will be expected to be the same whether hydrogen or any one of the alkali metals is chosen for the radical M, if the concentrations c_1 and c_2 are the same in each case and below about 0.05 *N*. The potential at each electrode is, of course, the result of the tendency of the electrode material to form chloride ions and the opposing tendency of the osmotic pressure of the chloride ions already in solution. The sum of the electrode potentials will thus be determined by the difference of the osmotic pressures of the chloride ions in the two solutions. This difference of osmotic pressure will, in all probability, be very nearly the same for dilute solutions of chlorides of univalent metals at corresponding concentrations, since the degrees of dissociation in dilute solution as determined by the conductivity method have been found to be the same for these substances. The correct expression for the potential of the liquid junction in cells of the above type is, therefore, one which will yield values for the sum of the electrode potentials which are independent of the nature of the cation. Jahn's¹ accurate work on concentration cells of hydrochloric acid, potassium chloride and sodium chloride is, fortunately, well adapted to a test of these conclusions.

Table I, which is self-explanatory, gives the result of the author's calculations, based on Jahn's data. The transference numbers are from Noyes and Falk's² compilation. It will be observed that in each group of cells, in which the solutions of electrolytes have the same concentrations, the calculated sums of the electrode potentials have the same value within a few tenths of a millivolt. This is true even though the liquid junction correction in the case of the hydrochloric acid cells is 40% of the total voltage and of opposite sign to that necessary for the sodium chloride solutions. The agreement is as close as can be expected from our present knowledge of the transference numbers. A similar agreement of the values of the sum of the electrode potentials when the salt

¹ *Loc. cit.*, p. 2286.

² *THIS JOURNAL*, 33, 1454 (1911).

TABLE I.—CALCULATION OF THE LIQUID JUNCTION AND ELECTRODE POTENTIALS OF CHLORIDE CONCENTRATION CELLS. (SILVER-SILVER CHLORIDE ELECTRODES.)

Substance.	Concentrations, Mols per liter.	Transference number of cathion.	E. M. F. of cell.	Liquid junction potential.	"Electrode potential" = E. M. F. — liquid junction potential.	Average deviation from mean, millivolts.
HCl.....	0.01665 0.001665	0.833	—0.09235	—0.03694	—0.05541	
NaCl.....	0.01673 0.001674	0.396	—0.04360	+0.01146	—0.05506	0.22
KCl.....	0.01670 0.001674	0.496	—0.05424	+0.00044	—0.05468	
HCl.....	0.03330 0.003329	0.833	—0.09162	—0.03664	—0.05498	0.25
KCl.....	0.03347 0.003347	0.496	—0.05403	+0.00043	—0.05447	
HCl.....	0.008315 0.001665	0.833	—0.06487	—0.02595	—0.03892	
NaCl.....	0.008364 0.001674	0.396	—0.03073	+0.00808	—0.03881	0.04
KCl.....	0.008329 0.001670	0.495	—0.03844	+0.00039	—0.03883	
HCl.....	0.006686 0.001665	0.833	—0.05614	—0.02245	—0.03369	
NaCl.....	0.006686 0.001674	0.396	—0.02652	+0.00697	—0.03349	0.08
KCl.....	0.006700 0.001670	0.495	—0.03330	+0.00034	—0.03364	

TABLE II.—CALCULATION OF THE LIQUID JUNCTION AND ELECTRODE POTENTIALS OF CHLORIDE CONCENTRATION CELLS. (CALOMEL ELECTRODES.)

Substance.	Concentrations, Mols per liter.	Transference number of cathion.	E. M. F. of cell.	Liquid junction potential.	"Electrode potential" = E. M. F. — liquid junction potential.	Average deviation from mean, millivolts.
KCl.....	0.01999 0.01000	0.496	—0.01608	+0.00013	—0.01621	0.06
NaCl.....	0.02000 0.01000	0.395	—0.01293	+0.00339	—0.01632	
KCl.....	0.03000 0.01000	0.496	—0.02561	+0.00020	—0.02581	0.07
NaCl.....	0.03003 0.01000	0.396	—0.02056	+0.00538	—0.02594	
KCl.....	0.05009 0.02000	0.496	—0.02125	+0.00017	—0.02142	0.17
NaCl.....	0.05007 0.02000	0.396	—0.01670	+0.00437	—0.02108	

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF NITROGEN COMPOUNDS.

By GILBERT N. LEWIS AND ELLIOT Q. ADAMS.

Received July 19, 1915.

No other forms of elementary nitrogen are known to exist except the gas N_2 and its liquid and solid modifications. As in the case of oxygen and hydrogen, we shall postpone, for the present, the calculation of the free energy of liquid and solid nitrogen. Undoubtedly, at very high temperature, nitrogen would dissociate into the monoatomic gas, but it has been shown by Langmuir¹ that at $3500^\circ A$, a temperature at which hydrogen is largely monoatomic, nitrogen at atmospheric pressure shows no sign of dissociation, although dissociation to the extent of 5% would have been noticeable.

Concerning a large number of the important compounds of nitrogen we have information which enables us to calculate their free energies. Of the oxides there is only one, N_2O , which enters into no known reversible reaction which permits the calculation of its free energy. In the case of N_2O_3 and N_2O_5 equilibria are known which would permit the calculation of the free energy, but these have not yet been sufficiently studied. Of the compounds of hydrogen and nitrogen only one has been sufficiently investigated, namely, ammonia.

Ammonia.

$\frac{3}{2}H_2 + \frac{1}{2}N_2 = NH_3(g)$.—The equilibrium between ammonia and its elements has been fully studied, chiefly in the laboratories of Haber and of Nernst. The most recent and reliable investigations are those of Jost² and of Haber and Le Rossignol.³ The data obtained by these investigators will be considered after we have obtained the general free energy equation.

From the specific heat formulae given by Lewis and Randall,⁴

$$H_2; C_p = 6.50 + 0.0009T$$

$$N_2; C_p = 6.50 + 0.0010T$$

$$NH_3; C_p = 7.5 + 0.0042T$$

$$\Delta F = -5.5 + 0.00235T$$

In this case the same heat of reaction was found by Thomsen and by Berthelot, namely, $\Delta H_{298} = -12200$ cal.; hence $\Delta H_0 = -10700$, and

$$\Delta F^\circ = -10700 + 5.5T \ln T - 0.001175T^2 + 1T.$$

The results of the equilibrium measurements of Jost and of Haber and Le Rossignol are given in Tables I and II. Of the latter measurements

¹ Langmuir, *THIS JOURNAL*, **34**, 860 (1912).

² Jost, *Z. anorg. Chem.*, **57**, 414 (1908).

³ Haber and Le Rossignol, *Z. Elektrochem.*, **14**, 181 (1908).

⁴ Lewis and Randall, *THIS JOURNAL*, **34**, 1128 (1912).

some were made at 30 atmos. (marked *) and the rest at atmospheric pressure. In each table the first column gives the absolute temperature; the second gives $-\log K_p$, where $K_p = [\text{NH}_3]/[\text{H}_2]^{1/2}[\text{N}_2]^{1/2}$, and the last column gives the values of I calculated from these data with the above formula.

TABLE I.

Jost.		
T.	$-\log K_p$	I.
958	3.262	-10.50
1082	3.577	-10.89
1109	3.653	-10.88
1149	3.771	-10.83
1193	3.878	-10.83
1273	4.009	-11.07
1313	4.085	-11.09

TABLE II.

Haber and Le Rossignol.

T.	$-\log K_p$	I.
973*	3.167	-11.20
1023	3.330	-11.21
1074*	3.449	-11.37
1074	3.478	-11.24
1123	3.554	-11.51
1174*	3.672	-11.57
1203	3.699	-11.77
1273	3.830	-11.88

The agreement between the several values of I is not completely satisfactory. Both sets of measurements show a decided trend in I and it is difficult to judge whether this is due to experimental error or to errors in the values of ΔH_0 and of ΔT which we have chosen, although it is to be pointed out that the difference in one set of measurements at the extreme temperatures is no greater than the difference between the two sets at one temperature. Owing to the trend we shall choose a value of I somewhat lower than the mean and write

$$\Delta F^\circ = -10700 + 5.5T \ln T - 0.001175T^2 - 11.0T \quad (1)$$

Hence $\Delta F^\circ_{298} = -4740$, a value which may be in error by several hundred calories.

$\text{NH}_3(\text{g}) = \text{NH}_3(\text{l})$.—Owing to the great importance of liquid ammonia as a solvent it is desirable to calculate its free energy also. The vapor pressure of liquid ammonia at 25° is 9.8 atmos. according to the tables of Regnault and of Pictet. If ammonia were a perfect gas the increase in free energy in this reaction would be $-RT \ln (l/p) = 1350$, but, while the deviation of ammonia from the gas law may be sufficiently small at one atmosphere to warrant our ignoring it for the present, this is not the case between 1 and 10 atmospheres. Unfortunately the compressibility data for ammonia are meagre, but we are able to make a rough estimate for $\int v dp$ between 1 and 9.8 atmos., which leads to a result about 100 cal. less than the one given above on the assumption of the gas laws. We shall therefore write $\Delta F^\circ_{298} = 1250$. (2)

$1/2\text{H}_2 + 1/2\text{N}_2 = \text{NH}_3(\text{l})$.—Combining (1) and (2), $\Delta F^\circ_{298} = -3490$. (3)

$\text{NH}_3(\text{g}) = \text{NH}_3(\text{aq})$.—Ammonia solutions appear to obey Henry's Law over a wider range of concentration than might have been expected. According to the very consistent measurements of Gaus, of Abegg and

Riesenfeld, and of Locke and Forssall¹ at 25°, the constant $K = C/p$, where C is mols per liter and p is pressure in atmospheres, varies only very slightly between $C = 1$ and $C = 0.1$, and the limiting value at $C = 0$ is 56.7 with a probable error of about 1%. Hence, $\Delta F_{298} = -R'T \ln K = -2390$. (4)

$\frac{1}{2}H_2 + \frac{1}{2}N_2 = NH_3(aq)$.—Adding (1) and (4) gives $\Delta F_{298} = -7130$. (5)

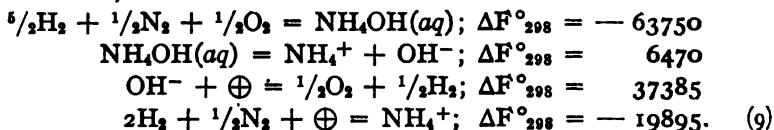
$NH_3(aq) + H_2O(l) = NH_4OH(aq)$.—As has been pointed out in the case of carbonic acid,² it is entirely immaterial, from a thermodynamic point of view, whether in dilute solution we consider a substance as hydrated or unhydrated. Provided, therefore, that we neglect the difference in free energy between pure water and the water of the solution, it is evident that it is a mere matter of choice whether we write the equations involving $NH_3(aq)$ or $NH_4OH(aq)$, for in any such reaction as this we may write $\Delta F^\circ = 0$. (6)

$\frac{5}{2}H_2 + \frac{1}{2}N_2 + \frac{1}{2}O_2 = NH_4OH(aq)$.—Combining Equations 5 and 6 with Equation 54 of the paper on Oxygen and Hydrogen Compounds,³ we find $\Delta F_{298}^\circ = -63750$. (7)

Ammonium Ion.

$NH_4OH(aq) = NH_4^+ + OH^-$.—The dissociation constant of ammonium hydroxide at 25° is given by Noyes and Kanolt⁴ as 18.1×10^{-4} , whence $\Delta F_{298}^\circ = 6470$. (8)

$2H_2 + \frac{1}{2}N_2 + \oplus = NH_4^+$.—We may combine Equations 7 and 8 with Equation 38 of the previous paper on oxygen and hydrogen compounds. Thus,



Oxides of Nitrogen.

$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$.—One of the most important of technical gas reactions is the direct union of oxygen and nitrogen in the electric arc. Haber has expressed the conviction that the equilibrium obtained in the arc is not a purely thermal equilibrium, but that some of the electrical energy is in some way utilized directly to produce a larger yield of nitric oxide than corresponds to the temperature. However this may be, it is evident that experiments with the electric arc alone could hardly give sufficiently accurate results for a free energy calculation. Nernst⁵

¹ See Abegg, *Handbuch anorg. Chem.*

² Lewis and Randall, *THIS JOURNAL*, 37, 466 (1915).

³ Lewis and Randall, *Ibid.*, 36, 1969 (1914).

⁴ Noyes, "The Electrical Conductivity of Aqueous Solutions," *Carnegie Institution Publications*, p. 290 (1907).

⁵ Nernst, *Z. anorg. Chem.*, 49, 213 (1906).

carried out, over a wide range of temperature, measurements of the amount of NO produced by heating air at atmospheric pressure to a given temperature for a sufficient time to establish equilibrium.

The free energy equation in this case is extremely simple, since we have taken the same formula for the heat capacities of N_2 , NO and O_2 , $\Delta F = 0$. $\Delta F^\circ = \Delta H_0 + IT$. ΔH for this reaction is given both by Thomsen and by Berthelot as 21600 cal., which is independent of the temperature. The equilibrium measurements of Nernst are given in Table III, where the first column gives the absolute temperature, the second the percentage by volume of NO in equilibrium with air at one atmosphere, the third, $K_p = [NO]/[N_2]^{1/2}[O_2]^{1/2}$ and the fourth the constant I.

TABLE III.

T.	Per cent. NO.	K_p .	I.
1811	0.37	0.0092	-2.59
1877	0.42	0.0105	-2.55
2033	0.64	0.0161	-2.40
2195	0.97	0.0246	-2.47
2580	2.05	0.0539	-2.56
2675	2.23	0.0590	-2.44

Mean, -2.50

Thus $\Delta F^\circ = 21600 - 2.50T$; $\Delta F^\circ_{298} = 20850$. (10)

$NO + \frac{1}{2}O_2 = NO_2$.—Nitrogen dioxide, according to the density measurements of Richardson,¹ dissociates appreciably above $150^\circ C$. into nitric oxide and oxygen. Table IV gives in the first column the absolute temperatures, in the second the percentage of NO_2 dissociated, as calculated from the density, in the third $R' \ln K_p$, where $K_p = [NO_2]/[NO][O_2]^{1/2}$, and in the fourth the values of I obtained from the equation which we are about to write.

TABLE IV.

T.	Per cent. dissoci.	$R' \ln K_p$.	I.
457	5	9.58	-0.3
552	13	6.60	-1.9
767	56.5	1.01	-2.5

Assuming that the heat capacity of NO_2 obeys the same equation as that of CO_2 , then for this reaction $\Delta F = -2.75 + 0.0056T - 0.00000186T^2$. The heat of this reaction calculated from Thomsen's measurements is given as 13450 cal. in Abegg's Handbuch, while the value 11000 is calculated by the equation of van't Hoff from the last two data of Table IV. We may take as a rough average 12000 cal. at ordinary temperatures, corresponding to $\Delta H_0 = -11400$. Taking the mean of the last two values of I, since the first is subject to much larger experimental error,

¹ Richardson, *J. Chem. Soc.*, 51, 397 (1887).

$\Delta F_0 = -11400 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 - 2.2T$ (11)
and $\Delta F^\circ_{298} = -7600$. This is an illustration of a reaction which is accompanied by a comparatively small free energy change and nevertheless takes place rapidly.

$\frac{1}{2}N_2 + O_2 = NO_2$.—Adding Equations 10 and 11

$$\Delta F^\circ = 10200 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 - 4.7T \quad (12)$$

$$\Delta F^\circ_{298} = 13250.$$

$2NO_2 = N_2O_4$.—The equilibrium between nitrogen dioxide and tetroxide was one of the earliest to be studied from the thermodynamic standpoint, and has been the subject of numerous publications. This is a case where the heat of reaction can best be determined from the equilibrium measurements themselves, although the value thus obtained is in good agreement with those obtained from a study of the specific heat.¹ Schreber² has made a critical summary of the dissociation constant calculated from the numerous measurements of the gas density. In accordance with this work, we shall take for the average value between 0° and 100° C., $\Delta H = -13600$. The heat capacity of 2 mols of NO_2 is doubtless greater than for one mol. of N_2O_4 , but since this reaction can be studied only over a small range of temperature, we shall regard ΔH as constant, and write

$$\Delta F^\circ = -13600 + 41.6T; \Delta F^\circ_{298} = -1200. \quad (13)$$

The value of I is obtained from the following table. The values of K_p are obtained by dividing 760 by the values of K_p given by Schreber.

TABLE V.

T.	K_p .	I.
273.0	65.0	41.5
291.3	13.8	41.4
322.9	1.25	41.7
346.6	0.296	41.6
372.8	0.075	41.6

$N_2 + 2O_2 = N_2O_4$.—Combining Equations 12 and 13 we find
 $\Delta F^\circ_{298} = 25300.$ (13a)

Nitrous and Nitric Acids and Their Ions.

Neither the free energy of nitric acid nor that of nitrous acid can be determined alone from any existing measurements of chemical equilibrium, but from the series of reactions considered below we may obtain equations which permit a simultaneous solution for both of these quantities.

$2AgNO_2(s) = Ag^+ + NO_2^- + Ag + NO(g)$.—Solid silver nitrite when heated, especially in the presence of water, decomposes to form silver nitrate, metallic silver and nitric oxide, Abegg and Pick³ showed that at 55° C. equilibrium in this reaction was established in a few days

¹ See Abegg's *Handbuch*, III-3, p. 135.

² Schreber, *Z. phys. Chem.*, 24, 651 (1897).

³ Abegg and Pick, *Z. anorg. Chem.*, 51, 1 (1906).

that when the pressure of NO was 4.28 atmos. the concentration of nitrate was 0.179 M. The concentration was determined by a somewhat indirect method and on this account their results are subject to some uncertainty.

To check upon their measurements we have studied briefly the equilibrium at 100° C. A glass tube containing a solution of silver nitrate and silver nitrite was connected with a closed manometer sealed in the vapor of boiling water. The space between the solution and the manometer was swept out with pure nitric oxide before the sealed, and this space was made so small that the change in concentration of the silver nitrate in the reaction was in the nature of a small constant value at the end of the second hour. After all corrections were made, the pressure of NO was 8.53 atmos. at the concentration of silver nitrate was 1.10 M.

The apparatus was heated for three hours, the pressure of Thomsen and Berthelot, neglecting the small heat of solution of silver nitrate, $\Delta H = 21200$. Assuming this to be 25° and 100° C., and applying the van't Hoff equation, we find the concentration of NO at 25° C. which would be in equilibrium to be 0.162 atmos. from the experiment of Abegg in equilibrium with 1.10 M AgNO_3 to be 0.00637.

Therefore write:
 $0.179 \text{ M}) + \text{Ag} + \text{NO}(1 \text{ atmos.}); \Delta F_{298} = 1080.$
 $1.10 \text{ M}) + \text{Ag} + \text{NO}(1 \text{ atmos.}); \Delta F_{298} = 3000.$

To determine the free energy of dilution of silver nitrate, we point measurements of Roth¹ and of Raoult,² from 0.01 M to 0.14 M, the latter, which can be employed for dilution from freezing points, completely

$= \text{AgNO}_3 (0.1 \text{ M}); \Delta F_{298} = -90$
 $= \text{AgNO}_3 (0.1 \text{ M}); \Delta F_{298} = -1920.$
 with those above.

$\text{Ag} + \text{NO} : \Delta F_{298} = 990$
 Lewis and Merrett average $\Delta F_{298} =$
 on occasion, 990, for the corrected degree
 we have for the change from 0.1 M
 ion and nitrite $\Delta F = 2RT \ln$
 the normal free energy of the reaction

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$\text{AgNO}_2(s) = \text{Ag}^+ + \text{NO}_2^-$.—Abegg and Pick determining the solubility and the complex formation of silver nitrite obtained for the solubility product at 25° C., $(\text{Ag}^+)(\text{NO}_2^-) = 2.0 \times 10^{-4}$, whence $\Delta F^\circ_{298} = 5050$. (15)

$2\text{NO}_2^- + \oplus = \text{NO}_2^- + \text{NO}(g)$.—Combining (14), (15) and Equation 50 of a preceding paper¹ for the free energy of silver ion, $\Delta F^\circ_{298} = 12570$. (16)

$2\text{NO}_2^- + \oplus = \text{NO}_2^- + \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$.—Combining Equations 11 and 16, $\Delta F^\circ_{298} = -8280$. (17)

$\text{H}^+ + \text{NO}_2^- + 2\text{NO}(g) + \text{H}_2\text{O} = 3\text{HNO}_2(aq)$.—The reaction which occurs in the decomposition of aqueous nitrous acid is reversible. Nitric oxide at a definite pressure, in contact with a solution of nitric acid, leads to an equilibrium concentration of nitrous acid. This equilibrium was studied over a wide range of concentration by Saposhnikov² by passing nitric oxide through nitric acid solution and determining the amount of nitrous acid, either by analysis or by measurements of the conductivity of the solution at the beginning and end of the experiments. The latter method was also employed by Lewis and Edgar³ with the purpose of obtaining a more exact determination of the equilibrium constant. Starting with 0.1 *M* HNO_3 and passing NO through at approximately atmospheric pressure, they were able to determine the change of conductance with unusual exactness. In five experiments the decrease in conductance, which is itself a small fraction of the total conductance, showed an average deviation from the mean of less than one-half of one per cent. There is no doubt, therefore, that a definite equilibrium is established. Unfortunately, however, it is not certain that the measured conductance is an exact criterion of the concentration of nitric acid in the mixture which contains both HNO_2 and NO. If these substances, even to a small degree, change the conductivity, the calculation of the equilibrium constant will be largely affected.

According to the measurements of Lewis and Edgar, the solution originally 0.1 *M* with respect to nitric acid becomes, in equilibrium with NO at 0.961 atmos., 0.0830 *M* with respect to nitric acid,⁴ 0.0495 *M* with respect to undissociated nitrous acid. Assuming that the corrected degree of dissociation of HNO_2 at this concentration is 0.74 we find for the equilibrium constant, $K = (\text{HNO}_2)^2/(\text{H}^+)(\text{NO}_2^-)[\text{NO}]^2 = 0.0346$.

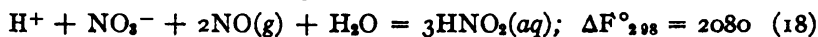
¹ Lewis and Randall, *THIS JOURNAL*, 36, 1983 (1914); $\text{Ag} + \oplus = \text{Ag}^+$; $\Delta F^\circ_{298} = 18424$.

² Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 32, 375 (1900); 33, 506 (1901).

³ Lewis and Edgar, *THIS JOURNAL*, 33, 292 (1911).

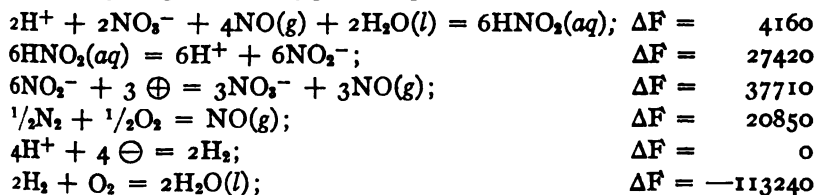
⁴ A careful reconsideration of the conductance data indicates that the value 0.0836 *M* should have been chosen as the concentration. Owing to other uncertainties it does not seem necessary to make this change.

Experiments by Lewis and Edgar with 0.2 *M* nitric acid, which were regarded as incomplete, but are nevertheless significant, give a considerably lower value of *K*. The values found for the concentrations of nitric and nitrous acid in equilibrium with NO at 0.969 atmos. were, respectively, 0.1785 and 0.0651. In so concentrated a solution the corrected degree of dissociation is hard to estimate. Assuming it to be 0.66, *K* = 0.0216. Saposhnikov's constants, when recalculated in terms of the corrected degree of dissociation, were 0.0320 at 0.05 *M*, 0.0268 at 0.1 *M*, and 0.0290 at 0.2 *M*. Since Saposhnikov used both conductivity and analysis we may give more weight to his measurements than their apparent accuracy would warrant. We probably shall not be far wrong in assuming as the final value *K* = 0.030, whence



$\text{HNO}_2(\text{aq}) = \text{H}^+ + \text{NO}_2^-$.—Owing to the instability of nitrous acid, its dissociation constant has not been determined with high accuracy, but there is apparently no large error in the determination of Schumann,¹ who measured the conductivities of freshly prepared mixtures of equivalent solutions of sodium nitrite and hydrochloric acid. He found $K_{298} = (\text{NO}_2^-)(\text{H}^+)/(\text{HNO}_2) = 0.00045$. Hence $\Delta F^\circ_{298} = 4570$. (19)

$\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{O}_2 + \ominus = \text{NO}_3^-$.—From the equations which have so far been obtained it is possible to determine the free energy of formation of both nitrate and nitrite ion. Ordinarily it is possible to determine the free energies of a series of compounds one by one, but in this case it is impossible from the reactions which have been studied to obtain the free energy of either nitrate or nitrite ion without accumulating data which suffice for the determination of the other. In other words, we have equations which are to be solved simultaneously for two unknown quantities. In order to find the free energy of formation of NO_3^- we shall combine Equations 18, 19, 16 and 10 of this paper with Equations 8 and 53 of the paper on hydrogen and oxygen compounds.²



Hence by addition



$\frac{1}{2}\text{N}_2 + \text{O}_2 + \ominus = \text{NO}_2^-$.—Subtracting 17 from 20 and dividing by two, $\Delta F^\circ_{298} = -7410$. (21)

¹ Ber., 33, 527 (1900).

² Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{N}_2 + \text{O}_2 = \text{HNO}_2(\text{aq})$.—Combining Equations 21 and 19, and taking once more the free energy of formation of H^+ equal to zero, $\Delta F^\circ_{298} = -11980$. (22)

It is to be noted that Equations 20, 21 and 22 all depend upon Equations 18 and 19, which are open to some question. It seems, therefore, extremely desirable to obtain by a different method an equation connecting the free energy of nitrate and nitrite ions. Experiments which we now have under way promise a more accurate determination of these free energies.

We wish to express our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the various compounds of nitrogen considered in this paper:

Substance.	F°_{298}	Equation.	Substance.	F°_{298}	Equation.
$\text{NH}_3(\text{g})$	— 4740	1	$\text{NO}(\text{g})$	20850	10
$\text{NH}_3(\text{l})$	— 3490	3	$\text{NO}_2(\text{g})$	13250	12
			$\text{N}_2\text{O}_4(\text{g})$	25300	13a
$\text{NH}_3(\text{aq})$	— 7130	5	NO_2^-	—23100	20
$\text{NH}_4\text{OH}(\text{aq})$	—63750	7	NO_3^-	— 7410	21
NH_4^+	—19895	9	HNO_2	—11980	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF FORMATION OF FORMIC ACID.

BY GERALD E. K. BRANCH.

Received July 19, 1915.

Introduction.

As a first step toward the preparation of a set of free energy tables for organic substances it is important to determine the free energy of formation from their elements of a few typical organic compounds. This has been accomplished in the case of one important compound through the study of the reversible synthesis of urea by Lewis and Burrows.¹ Formic acid is another simple organic compound whose free energy of formation may be obtained by a similar method.

It is well known that formic acid decomposes on heating into carbon monoxide and water, and also that sodium formate is obtained by the action of carbon monoxide on sodium hydroxide. Preliminary experiments showed that formic acid is produced in small amounts on heating water and carbon monoxide together. It is therefore apparent that the synthesis of formic acid from carbon monoxide and water is reversible.

¹ THIS JOURNAL, 34, 1515 (1912).

The most satisfactory condition for the accurate measurement of this equilibrium was obtained by heating dilute solutions of formic acid in closed vessels.

Experimental Method.

The apparatus consisted of a reaction tube, A, connected as shown in Fig. 1, to a capillary tube, B, in which a bulb, C, had been blown (both capillary tube and bulb being calibrated), in such a manner that it could be immersed in the vapor bath, D. To the reaction tube a small tube, E, was sealed. The apparatus was made of quartz.

Mercury was then introduced, so as to fill the connecting tube completely, the capillary tube to a graduation mark below the bulb, and the reaction tube to a height sufficient to prevent any of the solution from leaving it at the highest pressures reached. The tip of the capillary tube, which had been previously drawn out to a fine point, was quickly sealed, thus forming a manometer capable of measuring high pressures.

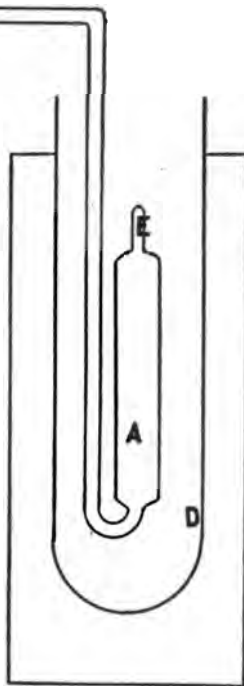


Fig. 1.

The reaction tube was filled to the top of the tube E with the reaction mixture. Some of the solution in the tube E was then rapidly boiled out, and the tube sealed off. In this way air was excluded without altering the concentration of the solution. This was tested by analyzing a sample taken from a tube which had only been sealed. It showed no detectable difference in composition from the original solution. The amount of air left could be observed as a very small bubble, and in no case could have made a measurable difference in the final pressures, as the volume of the gas space formed during the experiment was very great in comparison.

The vapor bath consisted of a large tube, well insulated on the outside

with asbestos packing. The vapor at constant temperature was supplied from a pure liquid at the bottom of the tube, which was kept boiling vigorously by an electrical heater. The reaction tube was placed far down into the hot vapor, but well above the liquid. There was in no case noticeable temperature gradient in the vapor, except at heights well above the reaction tube. Bromobenzene and naphthalene were the substances used in the bath.

The gas which was formed was collected for analysis by breaking at the point of the tube E under rubber connections.

The manometer tube was calibrated by means of a mercury thread while the bulb was calibrated in terms of lengths of the manometer tube by weighing the mercury it could contain and comparing it to the weight of mercury contained in a known length of the manometer tube. The length of the air space was measured to a mark, and the space between this mark and the end of the tube was calibrated by means of a mercury thread. The difference in levels of the mercury column in the manometer and the reaction tube was calculated from the measured rise in the manometer tube and the fall in the reaction tube, calculated from the ratio of the diameters of the two tubes. A correction was also made for the capillary depression, which was determined by a rough experiment. The pressure of the CO was obtained by deducting the vapor pressure of the water from the total pressure.

The solutions contained known concentrations of formic acid, and in the later experiments of hydrochloric acid. These concentrations are expressed in mols per 1000 g. of solution. After the pressure was measured a weighed amount of the solution was titrated with a KOH solution using phenolphthalein as the indicator. After each titration the KOH was titrated against a standardized solution of HCl. The difference between the concentrations of acid before and after experiment gives approximately the number of mols of CO given off per 1000 g. of solution. From this value the change in the concentration of HCl was calculated in mols per 1000 g. The concentration of the HCOOH was then obtained from the difference.

Experimental Results.

Table I gives the results of an experiment in which a pure solution of formic acid was heated at 156°. It is evident that even after 14 days the reaction is still very far from equilibrium. A catalyst for the reaction was therefore sought. Hydrochloric acid was the first substance tried, with the idea that it might have the desired effect through the temporary formation of the unstable substance formylchloride. Although it is doubtful that this is the mechanism of its action, nevertheless it proved to be a very efficacious catalyst. This catalytic action is shown not only by hydrochloric acid but by all the mineral acids.

TABLE I.

Time.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 20.3°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0.....	131.7	20.3°	131.65	0	75.2
10 min.....	24.15	19.9°	24.2	8	417
1 day.....	22.6	20.8°	22.6	10	448
2 days.....	21.8	23.0°	21.6	10	468
3 days.....	20.45	21.0°	20.4	12	497
4 days.....	19.5	18.5°	19.6	13	518
5 days.....	18.65	20.0°	18.65	13	543
6 days.....	17.95	19.6°	18.0	14	564
7 days.....	17.2	19.3°	17.25	15	589
8 days.....	16.7	23.0°	16.55	15	603
9 days.....	16.35	28.0°	15.95	16	627
10 days.....	15.75	24.8°	15.5	16	655
11 days.....	15.1	21.5°	15.05	17	675
14 days.....	13.7	19.0°	13.75	19	739

The catalytic action is shown graphically in Fig. 2, in which the two curves show the rate of development of pressure through the formation of carbon monoxide in two experiments carried out under approximately similar conditions in the presence and absence of hydrochloric acid. The curve for the reaction when HCl was absent was drawn from the data

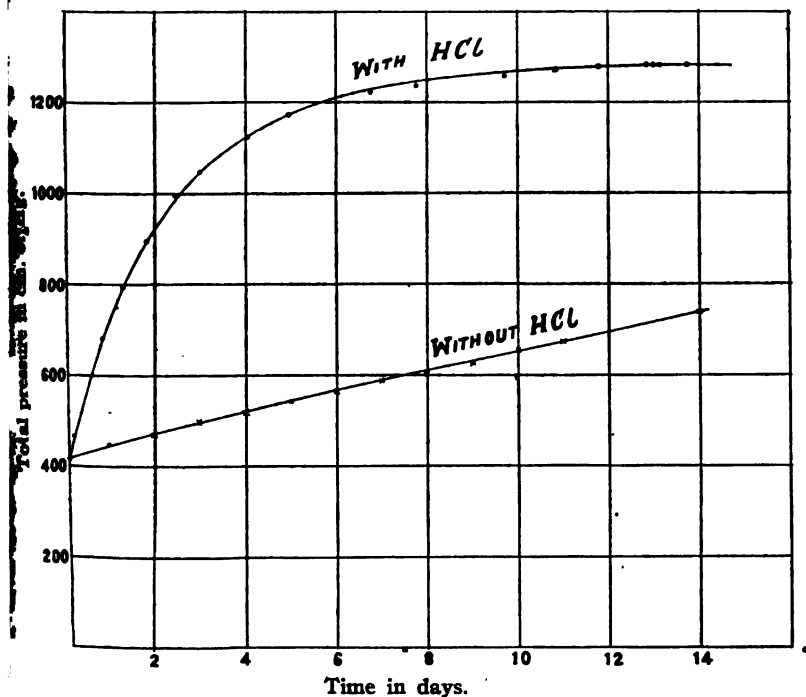


Fig. 2.

given in Table I, while the data for the other curve are given in Table II.

Tables II, III, IV, V and VI give the results obtained in the presence of HCl, and at the temperatures 156° and 218° .

Experiment 1.

TABLE II.

Temperature = 156.1° .

Time.		Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 16.9° C.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Hrs.	Min.					
0	..	235.9	16.9°	235.9	0	74.7
3	25	40.94	16.9°	40.94	33	463
20	20	27.59	15.0°	27.77	46.5	681
31	50	23.39	13.5°	23.67	50.5	795
44	..	20.80	14.7°	20.96	53	895
72	..	17.97	20.0°	17.79	55.5	1047
119	..	15.79	17.0°	15.78	58	1175
162	30	15.04	15.5°	15.12	58.5	1224
185	..	14.87	14.8°	14.98	59	1236
233	..	14.50	13.0°	14.70	59	1258
265	..	14.99	26.2°	14.52	58.5	1272
283	..	14.52	18.0°	14.46	59	1278
308	..	14.32	14.9°	14.42	59.5	1282
312	..	14.38	16.0°	14.42	59.5	1282
315	..	14.38	16.0°	14.42	59.5	1282
330	..	14.23	13.0°	14.42	59.5	1282

The pressure at equilibrium in this experiment is taken as 1282 cm. of Hg.

The solution originally contained 0.2523 mol of formic acid and 0.48 mol of HCl per 1000 g. of solution. After equilibrium had been reached 4.366 g. of the solution were equivalent to 58.66 cc. of a KOH solution and 87.59 cc. of this solution were equivalent to 39.60 cc. of 0.0995 N HCl. Hence the solution contained 0.1210 mol of HCOOH and 0.48 mol of HCl per 1000 g.

Experiment 2.

TABLE III.

Temperature = 156.1° .

Time.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 17° .	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0.....	234.1	17°	234.1	0	75.9
6 h. 15 m.....	37.81	17°	37.81	24	504
21 h. 30 m.....	28.38	21.4°	27.95	43.5	680
3 d. 18 h.....	17.73	16.5°	17.76	54.5	1054
4 d. 16 h.....	16.88	16°	16.93	55	1105
9 d.....	15.53	17°	15.53	56.5	1201
10 d.....	15.16	14°	15.32	57	1217
13 d.....	15.20	19°	15.10	57	1234
14 d.....	15.09	17°	15.09	57	1234
15 d.....	15.12	17.7°	15.08	57	1235

The pressure at equilibrium in this experiment is taken as 1234 cm. of Hg, the mean of the last three measurements.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 4.115 g. of the solution were equivalent to 55.07 cc. of a solution of KOH and 69.14 cc. of this solution were equivalent to 31.09 cc. of 0.0995 N HCl . Hence the solution contained 0.1162 mol of HCOOH and 0.4826 mol of HCl per 1000 g.

Experiment 3.

TABLE IV.

Temperature = 156.1°.

Time.	Air space in manometer in cm. in tube.	Temperature of air.	Air space calculated to 18°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0.....	231.7	18°	231.7	0	75.65
1st day ¹	14.91	17°	14.96	54.5	1226
2nd day.....	14.93	19°	14.88	54.5	1232
3rd day.....	14.97	20°	14.87	54.5	1233
4th day.....	14.97	20°	14.87	54.5	1233
7th day ²	14.51	22°	14.32	54	1278
8th day.....	14.71	21.5°	14.54	54	1260
9th day.....	14.94	22.3°	14.73	54.5	1244
11th day.....	15.16	25°	14.80	54.5	1238

The pressure at equilibrium in this experiment is taken as 1234 cm. of Hg, which is the mean of the values obtained on the 2nd, 3rd, 4th and 11th days.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 3.915 g. of the solution were equivalent to 45.10 cc. of a KOH solution, 38.30 cc. of which were equivalent to 20.00 cc. of 0.0995 N HCl . Hence the solution contained 0.1159 mol of HCOOH and 0.4826 mol of HCl per 1000 g.

Experiment 4.

TABLE V.

Temperature = 217.9°.

No. of reading.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 22.4° C.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Original.....	616.1	22.4°	616.1	0	75.2
1st ³	12.03	18.4°	12.20°	44	3842
2nd.....	12.03	18.6°	12.19	44	3845
3rd.....	12.02	19°	12.16	44	3854

Mean, 3847

¹ The preliminary heating was done in a cumene bath boiling at 163°.

² The tube had been heated in the cumene bath during the 6th day so that the equilibrium might be approached from both directions in this experiment.

³ The first reading was taken 4 hrs. after the mercury had become approximately stationary, and the three readings were taken over a period of three hours.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 0.6309 g. of the solution were equivalent to 26.56 cc. of a KOH solution, 85.14 cc. of which were equivalent to 11.63 cc. of 0.0995 N HCl . Hence the solution contained 0.0893 mol of HCOOH and 0.4829 mol of HCl per 1000 g.

Experiment 5.

TABLE VI.

Temperature = 217.9°.

No. of reading.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 25°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Original.....	619	25°	619	0	75.2
1st.....	15.02	23.1°	15.12	46	3125
2nd.....	14.94	21.9°	15.10	46	3129
3rd.....	14.90	21.0°	15.10	46	3129
4th.....	14.89	21.2°	15.08	46	3133
5th.....	14.94	21.8°	15.10	46	3129

Mean, 3129

In this experiment the concentration of formic acid was determined directly by oxidation in an alkaline solution with excess of KMnO_4 .

An excess of a standard solution of sodium oxalate was then added, and the solution acidified with sulfuric acid. The excess of KMnO_4 was titrated with the KMnO_4 solution, which was standardized against the oxalate solution.

After the experiment 1.213 g. of the solution were analyzed by the above method. 68.13 cc. of the KMnO_4 were added when 20.03 cc. of a 0.01 N sodium oxalate solution were used. 38.99 cc. of the KMnO_4 solution were equivalent to 20.03 cc. of the 0.01 N sodium oxalate. Hence the concentration of the HCOOH was 0.06170 mol per 1000 g. of solution. The original concentrations of HCl and HCOOH were the same as in the previous experiment, hence the concentration of HCl is 0.483 mol per 1000 g.

The partial pressure of CO were obtained by deducting the partial pressure of water from the total pressure. The pressures of HCOOH and HCl are negligible.¹ The water vapor was considered as that of a solution containing 1 mol² of foreign substance in 1000 g. of water. It can then be calculated by Raoult's law, $p = p_0 N_1$, where p is the partial

¹ The partial pressure of HCOOH calculated from its partial pressure at 25° given in this paper, was less than 0.1 cm. at 218°. The partial pressure of HCl over a 0.4 N solution at 218°, calculated from experiments at 100° given by E. G. Pierce (*J. Ind. Eng. Chem.*, Vol. 7, No. 3, p. 258), is 0.4 cm.

² This value cannot be calculated exactly owing to the lack of data for the degree of ionization of HCl at these temperatures; but an error of 10% corresponds to errors in the pressures of only 1 and 4 cm. of Hg at the lower and higher temperatures, respectively.

pressure of water over the solution, p_0 the vapor pressure of pure water, and N_1 the molal fraction of the water. $p_0 = 419^1$ cm. of Hg at 156.1° and 1668^1 cm. of Hg at 217.9° , $N_1 = 0.982$. Hence $p = 412$ cm. and 1638 cm. at the lower and higher temperatures, respectively.

The results of these experiments are given in Table VII. K , given in the sixth column, is the equilibrium constant of the reaction $\text{HCOOH}_{1M} = \text{H}_2\text{O}_{\text{liquid}} + \text{CO}$. It is the pressure of the CO in atmospheres, divided by the concentration of the HCOOH, and multiplied by the ratio of the fugacity of the water to the fugacity of pure water.² The concentrations in this table are all expressed in mols per 1000 g. of water.

TABLE VII.

Expt.	Temperature.	Concentration of HCl in mol per 1000 g. of H_2O .	Concentration of HCOOH in mol per 1000 g. of H_2O .	Pressure of CO in atmospheres.	K .
1.....	156.1°	0.4949	0.1239	11.45	90.8
2.....	156.1°	0.4940	0.1189	10.82	89.3
3.....	156.1°	0.4940	0.1186	10.82	89.6
4.....	217.9°	0.4936	0.0913	29.06	313
5.....	217.9°	0.494	0.06299	19.62	306

Mean value of $K = 89.9$ at 156.1° and 310 at 217.9° .

The reaction was shown to reach true equilibrium by heating at a higher temperature and so forming a higher pressure of CO. On heating again at the original temperature the pressure returned to the original value. This is shown in Table IV.

The reaction $\text{HCOOH} = \text{H}_2\text{O} + \text{CO}$ goes with no appreciable side reactions, as the gas formed is shown by the following analyses to be almost pure CO:

One sample of the gas collected from the reaction at 156.1° measured 12.18 cc. before absorption of the CO_2 , and 12.18 cc. after absorption.

Another sample measured 12.65 cc. before absorption and 12.70 cc. after absorption of the CO_2 . 6.1 cc. of this gas were made up to 14.40 cc. with oxygen and exploded. After explosion the volume was 11.35 cc. After absorbing the CO_2 formed the volume was 5.35. This corresponds to 98.4% CO and 0.5% H_2 . Slight admixture with air took place from the air in the rubber connections.

The gas obtained when the reaction was carried on at 217.9° also showed no decrease of volume on absorption with KOH. 36.72 cc.³ of a mixture of the gas and air were exploded. After the explosion the volume was 33.00 cc. After absorption of the CO_2 formed, the volume was 25.62

¹ Landolt-Börnstein-Roth, "Tabellen," 4th ed., p. 363.

² This ratio is taken as equal to the molal fraction, 0.982.

³ No measurement of the original volume was made as there was considerable accidental admixture with the air during the collection of the gas.

cc. These results correspond to the theoretical values for a mixture of 1 mol of CO to 0.003 mol of H_2 .¹

Free Energy at 25°.

The value of K at 25° C., or 298° A, was calculated from the equation $\ln K_2/K_1 = Q/R (1/T_1 - 1/T_2)$, where Q is the heat absorbed at constant pressure. This equation is only approximately true, as it assumes Q to be constant over the range of temperature considered. Substituting the values for K at 156.1° and 217.9°, and 1.989 for R , and 429.2 and 491 for T_1 and T_2 , respectively, we get $\ln 310/89.9 = Q/1.989 (1/429.2 - 1/491)$. Hence $Q = 8394$.² Similarly, $\ln 310/K_{298} = 8394/1.989 (1/298.1 - 1/491)$. Hence $K_{298} = 1.19$.

ΔF_{298} for the reaction $HCOOH (1 M) = H_2O(l) + CO(g)$ is given by the equation $\Delta F_{298} = -RT \ln K_{298}$, where $K_{298} = 1.19$. Hence $\Delta F_{298} = -1.989 \times 298.1 \times \ln 1.19 = -103 \text{ cal.} \approx 40 \text{ cal.}$

This is the free energy when the concentration of $HCOOH$ is an idealized one mol per 1000 g. of water, and in a solution containing about 0.49 mol of HCl per 1000 g. of water. However, an actual solution of $HCOOH$ of such a concentration is very nearly ideal. This can be shown by its agreement with Washburn's equation for the lowering of freezing points in aqueous solutions, $N = 0.0096895(\Delta T - 0.00425 \Delta T^2)$, where N is the molal fraction and ΔT the depression of the freezing point. This equation holds only when the solution is sufficiently dilute to be considered ideal. For formic acid when the concentration is 1.023 mols per 1000 g. of water, $\Delta T = 1.877$ and $N = 0.0181$,³ while from the formula $N = 0.01804$.

Fugacity of the Formic Acid.

In order to obtain ΔF for the decomposition of liquid formic acid it is necessary to know the ratio of the fugacities of $HCOOH$ in a solution of 1 mol to 1000 g. of water and in liquid formic acid. This was done by measuring the vapor pressure of formic acid over a solution identical with those used in the preceding experiments, except that the concentration of formic acid was increased in order to give a higher experimental accuracy.

The vapor pressure was obtained by bubbling a measured volume of air through a series of six tubes of the solution containing glass beads. These tubes were each connected to a larger bulb containing about 100 cc. of the solution so as to prevent any change in the concentration. The

¹ The small amounts of hydrogen given by these analyses were neglected, as they are probably chiefly errors in the analysis.

² On account of the extremely contradictory values obtained calorimetrically for the heat of formation of formic acid it, seemed inadvisable to attempt to use them in this calculation.

³ Abegg, *Z. physik. Chem.*, 15, 218 (1894).

HCOOH was absorbed in KOH and determined by oxidation with KMnO_4 , and the excess of KMnO_4 determined with sodium oxalate in acid solution. A tube containing cotton wool was placed between the solution and the absorbing bulbs to keep back the spray. Two determinations were made.

The solution used contained 0.508 mol of HCl and 0.8505 mol of HCOOH per 1000 g. of water. In the first determination the volume of gas was 18330 cc. 43.57 cc. of 0.01 *N* sodium oxalate and 51.22 cc. of KMnO_4 were needed. 45.02 cc. of the oxalate were equivalent to 42.82 cc. of the KMnO_4 solution. The formic acid was therefore equivalent to 10.28 cc. of 0.01 *N* sodium oxalate. Hence 0.0000514 mol of HCOOH passed over. This represents a partial pressure of HCOOH of 0.00522 cm. of Hg. The molal fraction of HCOOH in this solution is 0.01495, while that of the solution containing 1 mol of HCOOH and 0.49 mol of HCl per 1000 g. of water is 0.01754. The partial pressure of HCOOH over the latter solution would be 0.00612 cm. of Hg.

In the second experiment, using the same solution, the volume of gas was 17540 cc. 68.75 cc. of KMnO_4 and 32.81 cc. of 0.01 *N* sodium oxalate were needed. 33.05 cc. of the oxalate solution were equivalent to 53.15 cc. of the KMnO_4 solution. This corresponds to 0.0000497 mol of HCOOH, or a partial pressure of 0.00527 cm. of Hg, corresponding to 0.00618 cm. of Hg for a solution 1 mol per 1000 g. The mean value is 0.00615 cm. of Hg.

The ratio of the fugacities of HCOOH in this solution to that in liquid HCOOH is equal to the ratio of partial pressures of HCOOH. For liquid HCOOH the partial pressure is 4.25 cm. of Hg at 298°.¹

ΔF_{298} for the change $\text{HCOOH}(l) = \text{HCOOH}(1 M)$ is therefore $-RT \ln 4.25/0.00615 = -3876 \approx 10$ cals.

Free Energy of Formation of Formic Acid.

Since for the reaction $\text{HCOOH}(l) = \text{HCOOH}(1 M)$ $\Delta F_{298} = -3876$ cals., and for $\text{HCOOH}(1 M) = \text{H}_2\text{O}(l) + \text{CO}$, $\Delta F_{298} = -103$ cals. For the reaction $\text{HCOOH}(l) = \text{H}_2\text{O}(l) + \text{CO}$, $\Delta F_{298} = -3979 \approx 50$ cals., or for $\text{H}_2\text{O}(l) + \text{CO} = \text{HCOOH}(l)$, $\Delta F_{298} = 3980$ cals.

The change of free energy for the formation of H_2O and for CO from their elements have been calculated by Lewis and Randall,² ΔF_{298} for the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(l)$ is -56620 cals., and for $\text{C}_{\text{graphite}} + \frac{1}{2}\text{O}_2 = \text{CO}$, $\Delta F_{298} = -32560$. Hence for the reaction $\text{C}_{\text{graphite}} + \text{H}_2 + \text{O}_2 = \text{HCOOH}(l)$, $\Delta F_{298} = -85200$ cals.

Summary.

The decomposition of formic acid into carbon monoxide and water was found to be reversible, and to be catalysed by mineral acids.

¹ Landolt-Börnstein-Roth, "Tabellen," 4th ed., p. 817.

² THIS JOURNAL, 37, 466 (1915).

The equilibrium between carbon monoxide and water on the one hand, and formic acid dissolved in water containing hydrochloric acid on the other, was measured at 218° C. and at 156° C. The partial pressure of formic acid from a similar solution was also measured.

From these data, and those given by G. N. Lewis and M. Randall for the free energies of carbon monoxide and water, the free energy of formic acid was calculated.

In conclusion, I wish to express my indebtedness to Professor G. N. Lewis for valuable suggestions and assistance in the prosecution of this research.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF THE TULANE UNIVERSITY OF LOUISIANA.]

THE PHENOMENON OF PASSIVITY IN CONNECTION WITH FERROUS ALLOYS OF DIFFERENT COMPOSITION AND STRUCTURE.¹

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Received July 12, 1915.

Introduction.

The literature dealing with the phenomenon of passivity of iron has very little to say about the chemical composition of the samples used in the experiments and nothing to say about their physical structure. A careful examination of iron and steel from a metallographical point of view reveals the fact that there is a tremendous difference in its character, due to slight changes in chemical composition and to the method of treatment, whether mechanical or thermal or both.² The physical structure of a sample is dependent upon, and greatly influenced by, each of these factors. The study of its physical structure more often gives a sample's character than an ultimate chemical analysis, and it is therefore highly important that this factor be given due consideration in any study made upon commercial irons and steels. We were led to believe, therefore, that many of the apparently conflicting results recorded in experiments upon the passivity of iron and steel were due in part, at least, to the indistinct understanding of the nature of these differences, and that a study of the influence of these variables, if any, upon the phenomenon in a comparative way might lead to a more general conclusion as to its character.

The fact that iron will become passive has suggested at least a possible solution to the problem of corrosion. Cushman³ in a comparatively

¹ A paper read before the Section of Inorganic and Physical Chemistry, American Chemical Society, at the New Orleans meeting, April 2, 1915.

² Sauver, "Metallography of Iron and Steel," 1912.

³ Cushman and Gardiner, "Corrosion and Preservation of Iron and Steel," Cushman, U. S. Dept. Agric., *Bull.* 30, 29 (1907).

recent work states that "small quantities of inhibitive substances in boilers should be highly efficacious in preventing pitting." The inhibitive substances referred to are passivifying in character. In his work upon passivity of iron under boiler conditions, Byers¹ verifies Cushman's general conclusion, at least in so far as anodic conditions are concerned, and establishes the fact that iron (99.8%) can be made passive when the anode under steam boiler conditions. Byers also suggests the use of certain concentrations of potassium dichromate solutions in boiler waters as an inhibitor of corrosion. It, therefore, seemed of interest in this connection to study, in a comparative way, the behavior of irons and steels of known composition and structure when passivifying conditions were imposed, and if possible to make a statement which would be general for all classes of irons and steels.

Experimental.

Alloys Used in the Experiments.—We had at our disposal an unusually large collection of ferrous alloys. This material was prepared for Professor Rugan of Tulane University while research fellow in metallurgy in the University of Manchester, England, and contains a large variety of samples with carbon, silicon, manganese, sulfur, and phosphorus as variables. In addition, there were others which had been subjected to various thermal treatments with corresponding modifications in physical structure. We also secured a set of Carnegie Commercial steels from the open hearth process, ranging from 0.11% to 1.12% carbon, with manganese, sulfur, phosphorus fairly constant for the series. All these were normalized samples.

Comparative Study of Transition Points from Active to Passive when Samples were Made the Anode in a Definite Electrolyte, and in Different Electrolytes.—This study was carried out with the following points in view: first, to prove that samples of very different composition and structure could be made passive with a definite current density when the anode in an electrolytic cell, the other factors being constant; second, to determine the relative positions of the transition points, *i. e.*, current density required for passivifying, for the various samples; third, to study the influence of the various electrolytes upon the transition points; and fourth, to trace any relation between these transition points and the composition and structure of the samples.

The apparatus employed was essentially that used by Byers² in the experiments upon the influence of the magnetic field on the passive state of iron, with the exception of the electromagnet and the form of the electrodes. The anode was a highly polished button of iron having an exposed surface area of 3.45 sq. cm. A polished copper wire was wound

¹ THIS JOURNAL, 34, 1368 (1912).

² *Ibid.*, 32, 750 (1910).

tightly around the circumference of the button and extending out some 10 cm. to make connection with the external circuit. The whole surface of the iron and copper except that prepared for exposure was coated over completely with hard paraffine for insulation.

The electrodes were put in series with the current source, a rheostat, and a Weston ammeter reading directly to 0.01 of an ampere. A voltmeter was connected across the circuit between the electrodes. When the iron was active the voltmeter would indicate the small differences of potential between the electrodes, and the ammeter would show a varying amperage with the change in resistance; when the iron became passive there was a sharp rise in the voltmeter readings and a corresponding drop in the ammeter readings. At this point oxygen was liberated from the anode.

TABLE I.—SAMPLES WITH C AND SI AS VARIABLES, MN, S, AND P FAIRLY CONSTANT.

Sample.	Chemical composition.					Current density in amperes per 3.45 sq. cm. necessary for transition from active to passive condition.		
	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	5% nitric acid.	N sodium sulfate.
A.....	4.03	0.243	0.15	0.15	0.108	1.10	1.00	0.10
B.....	3.70	0.233	0.16	0.011	0.018	2.10	1.35	0.26
C.....	3.08	0.172	0.13	0.01	0.019	1.90	1.00	0.40
D.....	2.59	0.146	0.12	0.012	0.016	2.10	1.35	0.36
E.....	1.96	0.215	0.20	0.015	0.013	1.90	1.35	0.50
F.....	1.58	0.168	0.17	0.014	0.015	2.00	1.35
G.....	0.99	0.233	0.19	0.012	0.015	2.05	1.40	0.48
H.....	0.55	0.182	0.20	0.014	0.013	1.75	1.25	0.52
I.....	0.15	0.186	0.15	0.017	0.040	2.00	1.50

TABLE II.—SAMPLES WITH COMPOSITION AND HEAT TREATMENT AS VARIABLES.

Sample.	Chemical composition.					Transition densities.		
	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	5% nitric acid.	N sodium sulfate.
D.....	2.59	0.146	0.12	0.012	0.016	2.10	1.35	0.36
D11.....	2.59	0.146	0.12	0.012	0.016	2.15	1.35	0.50
D16.....	2.59	0.146	0.12	0.012	0.016	1.65	1.25	0.45
D26.....	2.59	0.146	0.12	0.012	0.016	2.00	1.25	0.50
E.....	1.96	0.215	0.20	0.015	0.013	1.90	1.35	0.50
E11.....	1.96	0.215	0.20	0.015	0.013	1.90	1.20	0.47
E16.....	1.96	0.215	0.20	0.015	0.013	1.85	1.25
E26.....	1.96	0.215	0.20	0.015	0.013	2.00	1.25	0.50
F.....	1.58	0.168	0.17	0.014	0.015	2.00	1.35
F11.....	1.58	0.168	0.17	0.014	0.015	2.00	1.75
F16.....	1.58	0.168	0.17	0.014	0.015	2.05	1.45
F26.....	1.58	0.168	0.17	0.014	0.015	2.10	1.50
I.....	0.15	0.186	0.15	0.017	0.040	2.00	1.50
I11.....	0.15	0.186	0.15	0.017	0.040	2.25	1.50
I16.....	0.15	0.186	0.15	0.017	0.040	2.25	1.50
I26.....	0.15	0.186	0.15	0.017	0.040	2.35	1.45

TABLE III.—SPECIAL SAMPLES WITH C, SI, AND HEAT TREATMENT AS VARIABLES.

Sample.	Chemical composition.					Transition densities.		
	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	N phosphoric acid.	N sodium sulfate.
J.....	4.60	0.79	0.126	0.016	0.018	1.50	0.34	0.52
J17.....	4.60	0.79	0.126	0.016	0.018	1.75
O.....	3.98	1.79	0.23	0.010	0.013	2.03	0.34	0.56
O2.....	3.98	1.79	0.23	0.010	0.013	1.71	0.55
P.....	3.79	2.96	0.25	0.010	0.012	1.57	0.37	0.57
P1.....	3.79	2.96	0.25	0.010	0.012	1.80	0.57
Q2.....	3.76	4.20	0.27	0.010	0.012	1.80	0.38	0.55
Q3.....	3.76	4.20	0.27	0.010	0.012	1.59	0.52
R1.....	3.79	4.83	0.30	0.010	0.012	2.02	0.57
R3.....	3.79	4.83	0.30	0.010	0.012	1.70
Si.....	3.38	6.14	0.30	0.010	0.013	2.92

TABLE IV.—CARNEGIE STEELS WITH CARBON AS THE PRINCIPAL VARIABLE.

Sample.	Composition.				Transition densities.		
	Per cent. C.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	N phosphoric acid.	0.5 N phosphoric acid.
T.....	0.11	0.36	0.011	0.038	2.38	0.31	0.28
U.....	0.24	0.45	0.016	0.040	2.17	0.34	0.27
V.....	0.47	0.50	0.013	0.033	2.38	0.32	0.27
W.....	0.60	0.38	0.011	0.033	2.17	0.35	0.27
X.....	1.04	0.42	0.048	0.035	2.38	0.30	0.25
Y.....	1.12	0.37	0.042	0.034	2.04	0.34	0.27
Z.....	0.20	High	High	2.24	0.30	0.25

Note: Where the single letter occurs—A, B, C, etc.—it refers to the original sample, and where the single letter occurs followed by numerals—D11, D16, D26, etc.—it refers to that many heat treatments where the sample has been heated above the critical range and allowed to cool properly the respective number of times indicated by the numerals.

The electrolytes used were: 10% nitric acid, 5% nitric acid, N phosphoric acid, 0.5 N phosphoric acid, N sodium sulfate. The results of these experiments are best understood by reference to the above tables.

The results conclusively prove that samples of iron of very different composition and structure can be passivified with a definite current density when the samples are made the anode in an electric circuit; they show that the passivifying current density is in no way related, at least in no simple way, to the chemical composition or structure of the samples; and they further show that the condition of passivity is intimately related to the passivifying electrolyte, and that current densities required to passivify in one electrolyte do not hold for others. The results of these experiments confirm the view that the phenomenon is very much more general than the work of others has shown.

Comparative Study of the Solution of Samples in 10% Sulfuric Acid at Current Densities below that Required for Passivifying.—These

experiments were carried out with the following points in view: first, to determine whether there was a gradual change from active to passive, revealing itself in the amount of iron dissolved in a given time, as the current density approached nearer and nearer the transition point; second, to determine, if possible, whether or not the general statement that passive iron does not dissolve appreciably holds for samples as heterogeneous as these under investigation; and lastly, to determine any relation that may exist between the amount of iron dissolved and that required by Faraday's law.

The apparatus used was essentially that described elsewhere in this paper. The samples were polished and reparaflined. The dissolved iron was determined by titration with 0.1 *N* potassium permanganate solution. The time of solution was five minutes and the amperage used was known to be below and approaching that required for passivifying. The electrolyte was 10% sulfuric acid. The results follow in tabular form.

The results are not conclusive. Nine out of fifteen samples reveal the fact that less iron goes into solution as we approach the transition point; some of the remaining reveal exactly the reverse condition, and some show irregularity of solution at different current densities. We believe, however, from the results that the phenomenon of passage from

TABLE V.—HEAT TREATED SAMPLES.

Sample.	Time.	Amperes.	Gram of iron in solution, actual.	Gram of iron in solution, calculated.	Difference
E.....	300 sec.	0.2	0.01906	0.0173	+0.0017
E.....	300 sec.	0.4	0.03490	0.0346	+0.0003
E.....	300 sec.	0.5	0.04511	0.04325	+0.00186
E11.....	300 sec.	0.2	0.01557	0.0173	-0.00173
E11.....	300 sec.	0.4	0.03544	0.0346	+0.0008
E11.....	300 sec.	0.6	0.05155	0.0519	-0.00035
E16.....	300 sec.	0.2	0.01611	0.0173	-0.00121
E16.....	300 sec.	0.4	0.03327	0.0346	-0.0014
E16.....	300 sec.	0.6	0.05319	0.0519	+0.0012
E26.....	300 sec.	0.2	0.01986	0.0173	+0.0025
E26.....	300 sec.	0.4	0.03812	0.0346	+0.0035
E26.....	300 sec.	0.6	0.05531	0.0519	+0.0034
D.....	300 sec.	0.2	0.01825	0.0173	+0.0009
D.....	300 sec.	0.4	0.03222	0.0346	-0.0024
D.....	300 sec.	0.5	0.03866	0.04325	-0.00459
D11.....	300 sec.	0.2	0.02953	0.0173	+0.0122
D11.....	300 sec.	0.4	0.03275	0.0346	-0.0019
D11.....	300 sec.	0.5	0.04027	0.04325	-0.00298
D16.....	300 sec.	0.2	0.01879	0.0173	+0.0014
D16.....	300 sec.	0.4	0.03275	0.0346	-0.0019
D16.....	300 sec.	0.5	0.03866	0.04325	-0.00459
D26.....	300 sec.	0.2	0.01611	0.0173	+0.0012
D26.....	300 sec.	0.4	0.03275	0.0346	-0.0019
D26.....	300 sec.	0.5	0.0397	0.04325	+0.0035

TABLE VI.—CARBON STEELS.

Sample.	Time.	Amperes.	Gram of iron in solution, actual.	Gram of iron in solution, calculated.	Difference.
T.....	300 sec.	0.1	0.01235	0.00865	+0.0097
T.....	300 sec.	0.2	0.01879	0.0173	+0.00149
T.....	300 sec.	0.3	0.02685	0.02738	-0.00147
U.....	300 sec.	0.1	0.01020	0.00865	+0.00155
U.....	300 sec.	0.2	0.01986	0.0173	+0.0025
U.....	300 sec.	0.3	0.02738	0.02595	+0.00143
V.....	300 sec.	0.1	0.0102	0.00865	+0.00155
V.....	300 sec.	0.2	0.01986	0.0173	+0.0025
V.....	300 sec.	0.3	0.02738	0.02595	+0.00143
W.....	300 sec.	0.1	0.01074	0.00865	+0.00209
W.....	300 sec.	0.2	0.01986	0.0173	+0.0025
W.....	300 sec.	0.3	0.02738	0.02595	+0.00143
X.....	300 sec.	0.1	0.01181	0.00865	+0.00317
X.....	300 sec.	0.2	0.0204	0.0173	+0.0031
X.....	300 sec.	0.3	0.02738	0.02595	+0.00143
Y.....	300 sec.	0.1	0.01449	0.00865	+0.00584
Y.....	300 sec.	0.2	0.01879	0.0173	+0.0014
Y.....	300 sec.	0.3	0.02792	0.02738	+0.00054
Z.....	300 sec.	0.1	0.02148	0.00865	+0.01283
Z.....	300 sec.	0.2	0.01933	0.0173	+0.0020
Z.....	300 sec.	0.3	0.03544	0.02738	+0.00806

Note: The plus sign indicates that more iron dissolved than was calculated according to Faraday's law, the minus sign indicating less.

active to passive is not an instantaneous change in properties, but a gradual adjustment toward a new condition of equilibrium. In regard to the second point involved, we found it exceedingly difficult to maintain the condition of passivity in acids when once the circuit was broken, and we are, therefore, not able to make a statement that heterogeneous samples do not dissolve when passive. The third point regarding the relation between the actual amount dissolved and that required by Faraday's law is also not clearly brought out. It was found that local action on the surface due to its heterogeneity materially influenced the amount of iron going into solution, and from the results we should judge that while the local action itself was less when the surface was under the influence of the external current, still the amount dissolved exceeded the value given by the law to such an extent that we believe local action plays an independent part in this process of solution. In other words, we may say that iron of this character goes into solution in other ways, when the anode in a circuit, than according to Faraday's law. We intend to repeat the experiment in electrolytes other than that used.

Comparative Study of Electrode Potentials of Certain Samples in Normal Nitric Acid and in Normal Sodium Sulfate.—The electrode potential of a metal immersed in an electrolyte is directly proportional to

its solution tension. This solution tension is a measure of the ability of a metal to go over into the ionic form, and since in passive metals this tendency is practically reduced to zero, a study of the electrode potentials of different samples ought to reveal a proportionality between these potentials and the ability of the samples to go into the passive state. This is equivalent to saying that those metals with low solution tension, and, therefore, low electrode potential, ought to go over into the passive state more easily than those with higher solution tension. The purpose of these experiments was to find any such relation and if possible to prove or disprove the supposition in connection with heterogeneous material.

The samples employed were those described elsewhere in this paper. The electrolytes used were normal nitric acid and normal sodium sulfate. A normal calomel electrode¹ was used as a basis for the electrode potential determinations. The apparatus was arranged after this order. The half cell was arranged in series with the electrode through the intermediate liquid and the electrolyte, and connected to a Wolff potentiometer. The potentiometer was arranged in such a way that a fall of potential of 0.0001 of a volt per ohm was established.

The results are tabulated below:

TABLE VII.

In N nitric acid.		In N sodium sulfate.	
Sample.	Single potential of electrode.	Sample.	Single potential of electrode.
A.....	-0.2003	A.....	-0.0993
C.....	-0.1707	C.....	-0.0677
D.....	-0.1357	D.....	-0.0183
D11.....	-0.1382	D11.....	-0.0667
D16.....	-0.1657	D16.....	-0.0457
D26.....	-0.1168	D26.....	-0.0460
E.....	-0.1170	E.....	-0.0177
E11.....	-0.1184	E11.....	-0.0157
E16.....	-0.1059	E16.....	+0.0333
E26.....	-0.1137	E26.....	+0.0293
H.....	-0.1217	H.....	+0.0463
J.....	-0.1377	J.....	-0.0387
O.....	-0.1280	O.....	-0.1127
P.....	-0.1112	P.....	+0.0093
Q.....	-0.0789	Q.....	+0.0973
R.....	-0.0714	R.....	+0.1073
S.....	-0.0787	S.....	+0.1603

On examination of the electrode potentials of A, C, D, E, E16, Q, and S in normal nitric acid and comparison of their transition densities in Tables I, II and III, we see a general tendency of the transition density to go higher as the electrode potentials get larger. The same general tendency is observed in the case of samples A, C, D, E, O, P, Q, R and

¹ Findlay, "Practical Physical Chemistry."

in normal sodium sulfate, in Tables I, II and III. It seems, therefore, that the original supposition that metals with low solution tensions passivify at a lower current density than those with high solution tensions is in general correct for this character of material, but the statement cannot be made more definite at this time.

Summary.

1. Samples of iron of very different composition and structure can be made passive when the anode is an electric circuit. The transition density from active to passive is not related in any simple way to the composition and structure of the samples. The nature and concentration of the electrolyte are factors in bringing about passivity in samples of the character of these just as for the pure metal.

2. We believe that the phenomenon is not an instantaneous change from active to passive, but a gradual adjustment toward a new condition of equilibrium, since in the majority of the experiments less iron goes into solution as the current density necessary for passivifying is approached. No statement can be made relative to the solubility of passive iron of this character, since the samples behaved normally, *i. e.*, when the circuit was broken the anode became active.

3. The current density required for passivifying increases with the electrode potential. In general, metals with low solution tension passivify at a lower current density than those with high solution tension.

NEW ORLEANS, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE.]

DETERMINATION OF THE SOLUBILITY OF SILVER NITRITE AND ITS DEGREE OF DISSOCIATION IN A SATURATED SOLUTION.

BY HENRY JERMAIN MAUDE CREIGHTON AND WILLIAM HILLIS WARD.

Received August 14, 1915.

The pure silver nitrite used in the following measurements was prepared as follows: To a solution of silver nitrate, a solution containing a 25% excess of potassium nitrite was added, the precipitated silver nitrite allowed to settle, the supernatant liquid then decanted off and the crystals washed several times with cold water. These crystals were then recrystallized twice from hot, distilled water, and finally dried between filter paper. In order to ascertain the purity of these crystals of silver nitrite, which were pale, lemon yellow in color, their silver content was estimated by analysis with standard ammonium thiocyanate solution, ferric alum being used as an indicator. The results obtained were as follows: (I), 70.05% Ag; (II), 70.08% Ag; (III), 70.07% Ag. The close agreement between these values and the theoretical (70.10% Ag) is indicative of the high degree of purity of the silver nitrite used in the following measure-

ments. Owing to the rapid action of light on silver nitrite, it was kept in brown bottles which were completely covered with black paper. That silver nitrite when so kept undergoes but slight decomposition is shown by the fact that a sample of the salt, at the end of two months, was found to contain 70.01% Ag, and a three-year-old sample, 69.04% Ag.

The solutions of pure potassium nitrite, employed in some of the experiments, were prepared by adding solutions of pure potassium chloride to hot solutions containing a slight excess of pure silver nitrite, the precipitated silver chloride being removed by filtration.

Measurements of the conductivity of silver nitrite were carried out at $25 \pm 0.01^\circ$, the temperature being maintained by means of an electrically heated and regulated thermostat. The resistances were measured by means of a drum form of Wheatstone bridge, the wire of which was accurate to 0.01%. The coils of the resistance box were accurate to 0.02%. The electrolytic cell was 3 cm. in diameter and 10 cm. high. The cell constant was determined with a standard solution of potassium chloride. The water employed in the preparation of the silver nitrite solutions was prepared by the method of Jones and Mackay,¹ and had a specific conductivity of $1.3\text{--}1.6 \times 10^{-6}$. The conductivity at 25° of silver nitrite at a number of different concentrations is given in Table I.

TABLE I.—CONDUCTIVITY OF SILVER NITRITE.

Dilution. ϕ .	Equiv. cond. Λ .	$\Lambda_\phi/\Lambda_\infty$.
37.13	78.25	0.63
50.14	84.45	0.68
74.26	95.90	0.77
100.28	102.53	0.82
148.52	109.9	0.88
200.56	115.0	0.93
297	122.0	..
401	125.1	..
594	129.8	..

For Λ_∞ , the value 124.2 has been used. This value has been calculated from the electrolytic mobility of the cation,² $l_{\text{Ag}} = 62.5$, and that of the anion,³ $l_{\text{NO}_2} = 61.7$, at 25° . From the rapidity with which the equivalent conductivity increases with dilution, exceeding the limiting value, Λ_∞ , at a dilution of 400, it is probable that hydrolysis of silver nitrite occurs.

In order to determine the solubility of silver nitrite, a large excess of the salt was placed in each of two bottles of 300 cc. capacity, which were three-fourths filled with "conductivity" water and closed with tight-fitting, glass stoppers. These bottles were agitated in a large thermostat,

¹ H. C. Jones, and E. Mackay, *Am. Chem. J.*, **19**, 283 (1897).

² Ostwald-Luther, *Phys. Chem. Messungen*, p. 481, 3rd edition.

³ F. Vogel, *Z. anorg. Chem.*, **35**, 403 (1903).

the temperature of which was kept constant within 0.02° , for at least fourteen hours at temperatures below 40° , and for several hours at higher temperatures. At the end of the period of agitation the bottles were removed from the stirring device and kept in the thermostat for two or three hours longer, in order to allow the finely divided silver nitrite to settle. About 25 cc. of each solution were then withdrawn through a small tube filled with glass wool into a pipet, and placed in Erlenmeyer flasks fitted with glass stoppers. At the higher temperatures, the pipet was surrounded with a hot water jacket, so as to prevent the silver nitrite from crystallizing out from the solution. The weights of the solutions removed were determined, and the weight of silver nitrite contained therein ascertained by analysis with ammonium thiocyanate. From the results obtained the solubility of silver nitrite in water, *i. e.*, the weight of silver nitrite in 100 g. of solution, was calculated. The change in the solubility of silver nitrite with temperature is given in Table II. The values in this table represent the means of at least two determinations which seldom differed by more than a few tenths of 1%.

TABLE II.—CHANGE IN SOLUBILITY.
Solubility.

Temperature. C°.	G. per 100 grams of solution.	Mols per 1000 cc. of solution.
1	0.1589	0.01031
15	0.2752	0.01788
25	0.4135	0.02693
35	0.6016	0.03903
51	1.0240	0.06654
60	1.3625	0.08855

The influence of the presence of a second electrolyte containing a mutual ion upon the solubility of another is governed by these laws: (1) In a saturated solution of a partially dissociated electrolyte, the concentration of the undissociated portion remains constant even when another dissociated substance is added. (2) The product of the active mass of the ions of the electrolyte remains constant even when another electrolyte having a mutual ion is added. These laws may be expressed mathematically as follows:

$$m_0 (1 - \alpha_0) = m (1 - \alpha);$$

$$(m_0 \alpha_0)^2 = m \alpha (m \alpha + x \alpha_1),$$

where m_0 and m represent the solubility of the first electrolyte before and after the addition of the second, α_0 and α the degree of dissociation of the first electrolyte before and after the addition of the second, α_1 the degree of dissociation and x the concentration of the second electrolyte in the mixture. In the foregoing equations, m_0 , m and x are expressed in mols per liter. If, therefore, to a saturated solution of an electrolyte there is added a second electrolyte, having either an anion or cation in

common with the first, it is evident from the foregoing that the equilibrium, existing between the undissociated molecules and the ions of the first electrolyte, will be displaced in such a way that a decrease in the solubility of the first electrolyte results; and, moreover, equimolar addition of the mutual anion or cation should bring about the same decrease in the solubility. In order to determine whether this conclusion holds for silver nitrite, measurements of its solubility in the presence of silver nitrate and in the presence of potassium nitrite have been carried out at 25°. The results of these measurements are recorded in Table III.

TABLE III.—EFFECT OF ADDED SALTS ON SOLUBILITY.

Conc. of AgNO ₃ or KNO ₃ in mols per liter.	Solubility of silver nitrite in the presence of				
	Silver nitrate.			Potassium nitrite.	
	G. per 100 grams of sol.	Mols per 1000 cc. of soln.		G. per 100 grams of sol.	Mols per 1000 cc. sol.
		Obs.	Calc.		
0.0000	0.4135	0.0269	..	0.4135	0.0269
0.00258	0.3991	0.0260	0.0259	0.3974	0.0259
0.00588	0.3735	0.0244	0.0247	0.3820	0.0249
0.01177	0.3432	0.0224	0.0227	0.3560	0.0232
0.02355	0.2943	0.0192	0.0187	0.3119	0.0203
0.04710	0.2498	0.0164	0.0139	0.2765	0.0181

As is to be expected, the results in the preceding table show that the addition of silver or nitrite ions brings about a decrease in the solubility of silver nitrite, and that the greater the concentration of these additions, the greater the decrease in the solubility of the salt. It will be observed, however, that although at the smaller concentrations equimolar additions bring about approximately the same decrease in the solubility of silver nitrite, as the concentration of the addition increases, the difference between the decrease in solubility brought about by each of the ions becomes more and more marked, reaching 10.4% when the concentration of the added salt is 0.0471 mol per liter.

By means of the preceding equations, it should be possible to calculate the solubility of silver nitrite in the presence of an electrolyte having a common ion. On solving the second of these equations for m , we obtain

$$m = -\frac{x\alpha_1}{2\alpha} + \sqrt{m_0^2 \left(\frac{\alpha_0}{\alpha}\right)^2 + \frac{x^2}{4} \left(\frac{\alpha_1}{\alpha}\right)^2}.$$

Since Nernst has shown¹ that in a mixture of two binary electrolytes of like strength (*e. g.*, salts of K, Na, NH₄, Ag, etc.), which have a common ion and concentrations c_1 and c_2 , respectively, the degree of dissociation is equal to and of the same value as that which would correspond to each alone for the concentration $(c_1 + c_2)$, accordingly, in the above equation $\alpha = \alpha_1$, and

¹ W. Nernst, *Z. physik. Chem.*, 4, 380 (1889).

$$m = -\frac{x}{2} + \sqrt{m_0^2 \left(\frac{\alpha_0}{\alpha}\right)^2 + \frac{x^2}{4}}.$$

This equation has been used to calculate the solubility of silver nitrite in the presence of the different concentrations of silver nitrate given in Table III, by employing for α_0 (the degree of dissociation of silver nitrite in a saturated solution), the value calculated from the conductivity data in Table I, *i. e.*, $\Lambda_{37.12}/\Lambda_{\infty} = 0.63$, and for α , values obtained by graphic interpolation of Kohlrausch's¹ values for the conductivity of silver nitrate, after converting them from 18° to 25°. As the values so calculated for the solubility of silver nitrite are very much smaller than those determined by experiment, it is probable that the value for α_0 calculated from conductivity data is much too low. The degree of dissociation of silver nitrite in a saturated solution has also been calculated by means of the equation expressing the constancy of the undissociated molecules,

$$\alpha_0 = \frac{m_0 - m + m\alpha}{m_0}.$$

The data employed for the calculation of α_0 and the values obtained are given in Table IV.

TABLE IV.— $m_0 = 0.0269$.

$m = a_1$	a_2	$a_1 + a_2$	$\alpha = a_1$	α_0
0.0260	0.00258	0.0286	0.89	0.894
0.0244	0.00588	0.0303	0.88	0.892
0.0224	0.01177	0.0342	0.87	0.892
0.0192	0.02355	0.0428	0.86	0.899
0.0164	0.04710	0.0635	0.85	0.909
				Mean, 0.90

In the above table, Col. 1 gives the solubility of silver nitrite in the presence of a concentration, c_2 , of silver nitrate. Col. 4 gives the degree of dissociation of silver nitrate corresponding to a concentration, $(c_1 + c_2)$. These values have been obtained from Kohlrausch's conductivity data for silver nitrate. The last column of the table records the values calculated for the degree of dissociation of silver nitrite in a saturated solution at 25°.

The mean value given above for α_0 has been used to calculate the solubility of silver nitrite in the presence of silver nitrate. The values obtained are recorded in Col. 4 of Table III, where it will be observed that these values agree fairly well with those determined by experiment. The large deviations between the calculated and experimental values of the solubility of silver nitrite, when the degree of dissociation α_0 is obtained from conductivity measurements, together with the constancy of the values for α_0 obtained from solubility data, indicate that it is very probable that the degree of dissociation of silver nitrite in saturated solu-

¹ Kohlrausch, F., *Wied. Ann.*, 26, 161 (1885).

tion is considerably higher than the value calculated from conductivity data. Using $\alpha_0 + 0.90$, the solubility product of silver nitrite at 25° is $L = 5.86 \times 10^{-4}$.

Summary.

1. Measurements have been made of the conductivity of aqueous solutions of silver nitrite at 25° . The results obtained indicate that hydrolysis of the salt takes place.

2. The solubility of silver nitrite has been determined at a number of temperatures between 1 and 60° .

3. The decrease produced in the solubility of silver nitrite by the addition of silver or nitrite ions has been measured at 25° . It has been found that equimolar quantities of these ions bring about approximately the same decrease in the solubility.

4. Calculations of the solubility of silver nitrite, in the presence of different quantities of silver nitrate, indicate that the degree of dissociation of silver nitrite in a saturated solution is considerably greater than is indicated by conductivity measurements.

5. From the data obtained in the solubility measurements, a mean value of 0.90 has been calculated for the degree of dissociation of silver nitrite in a saturated solution at 25° . Using this value, the solubility product of silver nitrite is 5.86×10^{-4} at 25° .

SWARTHMORE, PA.

THE DERIVATIVES OF PERCERIC OXIDE.

[FIRST PAPER.¹]

By C. C. MELOCHE.

Received July 21, 1915.

The preparation and analysis of a derivative of perceric oxide was first described by Cleve,² who found that perceric hydroxide corresponded to the oxide CeO_3 . In the same year Lecoq de Boisbaudran³ published a note confirming the conclusions of the former investigator. However, the work of von Knorre⁴ does not entirely substantiate the conclusions of Cleve, and Mengel⁵ agrees with von Knorre in his position. Pissarjewski⁶ has also contributed to the study of perceric hydroxide.

Methods for the preparation of a perceric potassium carbonate solution were first described by Job.⁷ He showed that the oxidation could be

¹ This paper is the abstract of part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the Degree of Doctor of Philosophy.

² *Bull. soc. chim.*, [2] 43, 53 (1885); *Jahrb. Fortsch. Chem.*, 1885, 491.

³ *Compt. rend.*, 100, 605 (1885); *Chem. News*, 51, 148 (1885); *Jahrb. Fortsch. Chem.*, 1885, 493.

⁴ *Z. angew. Chem.*, 1897, 723.

⁵ *Z. anorg. Chem.*, 19, 71 (1899).

⁶ *J. Russ. Phys. Chem. Ges.*, 32, 609 (1900); *Centr.*, [1] 1901, 86.

⁷ *Compt. rend.*, 128, 178, 1098 (1899); *Ann. chim. phys.*, [7] 20, 246, 253, 261 (1900).

effected by air as well as by hydrogen peroxide, and isolated the double compound. Baur¹ prepared crystals of perceric potassium carbonate by the third method described by Job, and concluded that the crystals obtained by this method had not been analyzed by Job. Baur on the basis of his analysis assigned the formula $\text{Ce}_2\text{O}(\text{CO}_3)_2\text{O}_3 \cdot 4\text{K}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ to the compound. Job gave to the crystals which he had prepared the formula $\text{Ce}_2\text{O}_3(\text{CO}_3)_3 \cdot 4\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$.

The use of alkaline cerous carbonate as a carrier for oxygen has been investigated to some extent by Job² and Baur.³ The absorption of oxygen by alkaline cerous solutions has been studied by Baur.⁴ An investigation of the autoxidation of cerous salts has also been conducted by Engler⁵ in connection with his work on the activity of oxygen.

Perceric Potassium Carbonate.

Reference was made above to Job's⁶ discovery of a double potassium perceric carbonate having the formula $\text{Ce}_2\text{O}_3(\text{CO}_3)_3 \cdot 4\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. He prepared this compound by the interaction of ceric ammonium nitrate and hydrogen peroxide in a strong solution of potassium carbonate. Cerous nitrate was also found to be suitable for this preparation.

Instead of working in strong potassium carbonate solution, as was done by Job, it has been found advantageous to pass a stream of carbon dioxide through the potassium carbonate solution until a large part of the potassium is removed as the bicarbonate. The filtered liquid, when kept at 5° for twenty-four hours, deposits ruby red crystals. The details of the method are as follows:

To 175 cc. of a saturated potassium carbonate solution 5 cc. of 30% hydrogen peroxide are added and then 13 g. of cerous ammonium nitrate dissolved in about 15 cc. of water are slowly added with stirring. The mixture is heated rapidly to 60° and kept at that temperature as long as the color of the solution deepens. As soon as the reaction is complete, carbon dioxide is passed through, and, after the temperature has decreased somewhat, the vessel is placed in cold water to which a piece of ice is added occasionally. The stream of carbon dioxide is continued until no further precipitation of potassium bicarbonate takes place. The mixture is then cooled to 0°, or slightly above, until as much as

¹ *Z. anorg. Chem.*, 30, 256 (1902); *Centr.*, [1] 1902, 1046.

² *Compt. rend.*, 134, 1052 (1902).

³ *Loc. cit.*, p. 253.

⁴ *Ber.*, 36, 3038 (1903); *Centr.*, [2] 1903, 931; *Ber.*, 37, 795 (1904); *Centr.*, [1] 1904, 991.

⁵ *Ber.*, 36, 2642 (1903); *Centr.*, [2] 1903, 547; *Ber.*, 37, 49 (1904); *Centr.*, [1] 1904, 566; *Ber.*, 37, 3268 (1904); *Centr.*, [2] 1904, 1280; C. Engler and J. Weissburg, "Kritische Studien über die Vorgänge der Autoxidation" (Braunschweig, 1904, Friedrich Vieweg und Sohn), p. 112.

⁶ *Loc. cit.*

possible of the potassium bicarbonate has crystallized out. Meanwhile, the passage of carbon dioxide is continued. Rapid filtration through glass wool is the best method for the separation of the potassium bicarbonate. Although part of the perceric compound seems to separate out in a finely divided form it is not retained by the glass wool. The filtrate is warmed to 40° and stirred, whereupon this finely divided material passes into solution. This solution is now passed through an asbestos filter to remove that portion of the original perceric precipitate which remains undissolved. The deeply colored liquid is covered and kept at about 5° for 24 to 48 hours. The separated crystals are thrown upon a Büchner funnel provided with a hardened filter and washed with a little ice water. The water is rapidly sucked off and the crystals are air dried by continuing the suction.

The analysis of the compound gave the following results:

	I.	II.	Av.	Ratio.		Theoret. comp.
				Det.	Probable.	
Ce.....	22.37	22.51	22.44	1.98	2	22.74
K ₂ O.....	30.98	31.21	31.10	4.09	4	30.56
CO ₂	21.42	21.37	21.40	6.03	6	21.39
O ¹	3.93	3.86	3.90	3.02	3	3.89
O ²	3.56	3.35	3.46	2.68	3	3.89
H ₂ O.....	17.74	17.70	17.72	12.20	12	17.52

The preceding results correspond to the formula $\text{Ce}_2\text{O}_4(\text{CO}_2)_{2.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The compound prepared by Job was $\text{Ce}_2\text{O}_3(\text{CO}_2)_{3.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The one prepared by Baur was $\text{Ce}_2\text{O}_4(\text{CO}_2)_{2.4}\text{K}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

The method of analysis was as follows: The cerium was precipitated as oxalate and weighed as CeO_2 according to the usual gravimetric method. The potassium of the filtrate was converted to the sulfate and weighed as such with the customary precautions. The carbon dioxide was determined gravimetrically by evolution and absorption in potassium hydroxide solution, sp. gr. 1.27. Sulfuric acid (1 : 5) was found to be best adapted for the decomposition. The method used for the determination of available oxygen was a modification of the one employed by Job. The procedure was as follows:

A small suction flask was fitted with a three-hole, tightly fitting, rubber stopper about one-quarter of an inch thick. A dropping funnel, a buret and a carbon dioxide delivery tube were attached. The side neck of the flask was made the outlet for carbon dioxide. About 1.2 g.³ of ferrous ammonium sulfate were weighed out and placed in the flask. Carbon dioxide which had been washed with water and dried by means of concentrated sulfuric acid was passed through the flask until all the air had been expelled. A small amount of cold boiled water just sufficient to dissolve the ferrous ammonium sulfate was added through the dropping funnel. After solution was complete 50 cc.

¹ Available oxygen.

² Unavailable oxygen, determined by difference.

³ On account of temperature conditions, etc., it will sometimes be necessary to use as little as 0.7 g. of ferrous ammonium sulfate and a correspondingly smaller amount of sample. In any case no more ferrous iron should be present than can be precipitated and redissolved by about 50 cc. of the sodium pyrophosphate solution.

of saturated sodium pyrophosphate solution was introduced. A precipitate was formed which, on shaking, redissolved in the excess of reagent. If this was not the case a little more sodium pyrophosphate was added. The 0.5 g. sample of potassium perceric carbonate, dissolved in 20 cc. of saturated potassium bicarbonate solution, was now added through the dropping funnel and followed by 10 cc. of the same potassium bicarbonate solution. The minimum amount of cold boiled water was used to wash the solution of cerium into the flask completely. Titration could then be effected by means of standard potassium permanganate solution from the buret. The end point was the first appearance of a faint yellow color, which is due to the oxidation of a small amount of cerium to the ceric condition. The standardization was conducted in exactly the same manner, except that no cerium was dissolved in the potassium bicarbonate solution. In this case, since no cerium was present, the end point was indicated by the first appearance of a faint pink color due to a slight excess of permanganate. Alkaline ferrous pyrophosphate solution is readily oxidized by gaseous oxygen, so that air must be rigidly excluded. The results obtained by this method were checked by an entirely different method to be described later.

The total water was determined by the direct method, that is, by heating in a current of dry air, absorbing the water in concentrated sulfuric acid and weighing. The unavailable oxygen was obtained by difference.

Perceric potassium carbonate parts with its water of crystallization readily. If left in a good desiccator over sulfuric acid or calcium chloride for only a few minutes the compound changes from a transparent ruby red to an opaque orange color. Exposure to air for any considerable length of time produces a similar effect.

The study of the mode of combination of the oxygen in the compound $\text{Ce}_2\text{O}_4(\text{CO}_3)_{1.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ presents many interesting features. For convenience we may classify the oxygen as follows:

(I) Three cerous oxygen atoms; (II) One ceric oxygen atom; (III) Two perceric oxygen atoms.

The three cerous oxygen atoms are unavailable. One of the remaining three atoms that are available¹ differs from the other two. All three are available in alkaline solution, but in acid solution a result is obtained which corresponds to one atom of available oxygen for every two atoms of cerium.

Job's method of determining total available oxygen presents the advantage that in the presence of considerable potassium bicarbonate no insoluble compounds are formed. No hydrated manganese dioxide is precipitated and the manganese of the permanganate is reduced to the divalent condition. However, on account of the peculiar nature of the perceric compound, it was thought desirable to study the total available oxygen by an altogether different method. The ordinary methods used for the determination of available oxygen are not applicable in this instance. As a matter of fact, the compound can not be dissolved in a mineral

¹ In the following discussion the word available will be applied to oxygen present in such form that it can be used efficiently for the wet oxidation of common reducing agents such as ferrous ammonium sulfate.

acid without complete decomposition and the liberation of two-thirds of its available oxygen in the gaseous state. The behavior of perceric

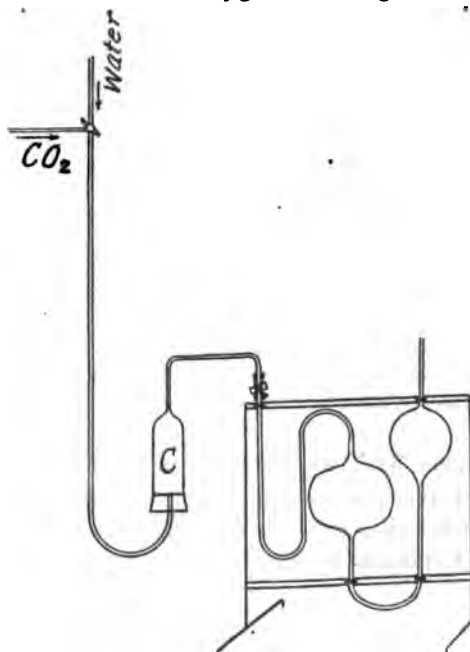


Fig. 1.

potassium carbonate toward acid ferrous sulfate and potassium iodide solutions will be discussed quantitatively later in this paper. The alternative method for the determination of the total available oxygen will be described first. The principle utilized is that the perceric compound on treatment with sulfuric acid in excess yields free oxygen. The remaining available oxygen can be determined by one of the usual methods, for example, by means of ferrous ammonium sulfate and potassium permanganate.

The determination of the free oxygen liberated on treatment with sulfuric acid was made in an apparatus (see

Fig. 1) constructed especially for the purpose. The details of the method are as follows:

About 0.5 g. of the potassium perceric carbonate was weighed out and placed in the decomposition cell *C*. The air was then displaced by a stream of carbon dioxide which had been washed with water and moist phosphorus. The decomposition cell was connected to a pipet containing 33 1/3% potassium hydroxide solution. Decomposition of the sample was accomplished by treating with an excess of sulfuric acid (1 : 3). The acid was admitted through the bottom of the cell under sufficient pressure to prevent the loss of gas through the inlet. The apparatus was so constructed that water could be admitted instead of the acid to force the gas into the absorption pipet. The carbon dioxide was first absorbed and the residue of oxygen returned to the gas buret and measured. Later, the oxygen was absorbed by means of alkaline pyrogallate solution in the regular manner. The small residue, presumably nitrogen, was returned to the buret, measured and subtracted.

The values obtained for the gaseous oxygen liberated when the compound $\text{Ce}_2\text{O}_4(\text{CO}_3)_{2.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ was treated with sulfuric acid in excess were:

% oxygen.....	2.554	2.505	2.557
Ratio of Ce : O in atoms.....	2 : 1.995	2 : 1.958	2 : 1.998

It is thus seen that when the above compound is treated as stated two atoms of oxygen are immediately and quantitatively evolved.

For the determination of the available oxygen which remains after treatment with dilute sulfuric acid, a separate sample was employed. The decomposition was first effected with a small amount (about 5 cc.) of dilute sulfuric acid (1:3). A weighed excess of ferrous ammonium sulfate was then dissolved in cold boiled water, acidified with sulfuric acid and added to the solution of the sample. The volume was then brought to about 200 cc. and the excess of ferrous ammonium sulfate titrated with potassium permanganate. The available oxygen remaining in solution was found to be as follows:

% oxygen.....	1.26	1.24
Ratio of Ce : O in atoms.....	2 : 0.98	2 : 0.97

These results, and those obtained above, show that when the potassium perceric carbonate is treated with dilute sulfuric acid two atoms of oxygen are evolved, while one atom remains in solution and is available for the oxidation of ferrous ammonium sulfate. The results obtained by this alternative method are in good agreement with those obtained by the ferrous pyrophosphate method. The ratio of the number of atoms of cerium to the number of atoms of total available oxygen is therefore 2:3 according to both methods.

It is of interest to note that the available oxygen remaining after treatment with dilute sulfuric acid is present in the form of hydrogen peroxide, as is shown by the addition of titanium sulfate solution. That the solution contains no ceric sulfate is indicated by the fact that it does not possess the bright yellow color characteristic of a ceric sulfate solution. The sulfuric acid solution of the compound under discussion not only oxidizes ferrous ammonium sulfate, but also reduces potassium permanganate solution, a further indication that the remaining available oxygen is present as hydrogen peroxide.

In this connection it is well to examine the results obtained by the ordinary methods for the determination of available oxygen. On the basis that part at least of the available oxygen was present in the form of combined hydrogen peroxide, a determination of the available oxygen was made by the iodimetric method modeled after the method of Kingzett for hydrogen peroxide. The concentrations were preserved as nearly as possible the same as in the Kingzett method, considering the fact that the perceric compound was dissolved in potassium bicarbonate solution.

The following was the method adopted: Two grams of potassium iodide were dissolved in 150 cc. of cold boiled water and 35 cc. of sulfuric acid (1 : 2) added, then, with constant stirring, 20 cc. of saturated potassium bicarbonate solution containing 0.5 g. of perceric potassium carbonate were added. About 30 cc. of wash water were required. After allowing to stand for 5 minutes the titration was made with sodium thiosulfate, using freshly prepared starch paste as indicator. One cc. of the sodium thiosulfate solution was equivalent to 0.0005055 g. oxygen. The results obtained were

% oxygen.....	1.34	1.34
Ratio of Ce : O in atoms.....	2 : 1.048	2 : 1.048

It will be observed that two-thirds of the available oxygen is not available by this method.

An attempt was also made to determine the total available oxygen by dissolving the sample in dilute (1:10) sulfuric acid containing a weighed excess of Mohr's salt and titrating the excess of the latter with potassium permanganate solution. The results obtained were discordant, but corresponded to somewhat over one atom of available oxygen for every two atoms of cerium.

Since the three available oxygen atoms in perceric hydrate can be determined by treating in the cold with a dilute sulfuric acid solution of ferrous ammonium sulfate and titration of the excess with potassium permanganate, it was thought that the double perceric potassium carbonate, after hydrolysis in the cold, might yield similar results by the same method, but the results obtained were very similar to those obtained above without previous hydrolysis.

The loss of about two-thirds of the oxygen may be regarded as a physical one. The above work indicates that it is impossible for perceric compounds to exist in a solution acid with a mineral acid such as sulfuric acid; also, the compound in contact with water alone undergoes rapid hydrolysis. It is therefore evident that, in the presence of acid, contact is necessary to make this oxygen available in the nascent form. The reason for the fact that a large portion of the oxygen is not available for wet oxidation is similar to the one which must also be assigned for the fact that large portions of the hydrogen are not available when certain of the metals are treated with dilute hydrochloric acid.

This loss of oxygen is, however, easily explained on a purely chemical basis. Ratios already given, the fact that after treatment with acid one oxygen remains in solution as hydrogen peroxide, and the other facts cited in the following, indicate that the equation representing the reaction under discussion may be written as follows:



The autoreduction, by which the oxygen is produced, is probably intramolecular, so that the oxygen is evolved in the molecular rather than in the atomic state.

That there are only two atoms of peroxide oxygen in the perceric complex seems reasonable from the following considerations: If three atoms were present more than one molecule of hydrogen peroxide would probably remain in solution after treatment with cold dilute sulfuric acid. If only one atom of peroxide oxygen were present, it is improbable that any hydrogen peroxide would remain after treatment with acid, since the following reaction takes place quantitatively:



The presence of peroxide oxygen is indicated qualitatively by the following reactions: When a 10% solution of the perceric potassium carbonate in 23% potassium carbonate solution was treated with a strong potassium carbonate solution of potassium ferricyanide, potassium permanganate, potassium manganate, potassium hypochlorite, or potassium hypobromite, a lively evolution of oxygen was observed. Likewise, when a 10% solution of the same compound in saturated potassium bicarbonate solution was treated with lead dioxide, oxygen was evolved. In this connection the structural formula which Engler¹ has suggested for Job's compound is of interest.

A very interesting property of perceric solutions which has not been mentioned above is their behavior toward hydrogen peroxide. The dark red-brown precipitate produced by the addition of this reagent corresponds possibly² to CeO_4 , but no detailed study of it has yet been made.

The remarkable stability of the double potassium perceric carbonates is one of their most interesting characteristics. This is illustrated by the comparative permanency of the potassium carbonate solution. The solution will keep for months with only slight decomposition. Such behavior is in marked contrast with that of a similar solution of hydrogen peroxide. As previously stated, the compounds part with their water easily. The remaining complex, however, can be heated for long periods above 110° without decomposition. Job³ states that by heating the compound $\text{Ce}_2\text{O}_3(\text{CO}_3)_{3.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ to 110° the compound $\text{Ce}_2\text{O}_3(\text{CO}_3)_{3.4}\text{K}_2\text{CO}_3$ was obtained free from water. It was still soluble in potassium carbonate solution and produced the characteristic blood-red coloration, and, furthermore, the available oxygen remained intact. This work would indicate that the peroxide oxygen is not combined as hydrogen peroxide. The compound $\text{Ce}_2\text{O}_4(\text{CO}_3)_{2.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ was desiccated and later heated for several hours to 110 – 120° . A test showed that after this treatment a little water still remained. The heating was then continued at 133 – 138° for two hours. A trace of water still remained, however. The dried material was for the most part soluble in potassium carbonate and yielded the characteristic blood-red solution. Two analyses gave for the content of available oxygen the following results:

(I) 4.35%

(II) 4.42%

The percentage required by theory for the anhydrous compound is 4.72%. It seems then that the process of drying at 133 – 138° is accompanied by the loss of small amounts of the available oxygen. In this case the loss was about 0.3%.

¹ *Ber.*, 36, 2642 (1903); Engler and Weissburg, *Loc. cit.*

² Job, *Ann. chim. phys.*, [7] 20, 261 (1900).

³ Job, *Ibid.*, [7] 20, 251 (1900).

Summary.

A different procedure for the preparation of perceric potassium carbonate has been described. The compound prepared by this method is somewhat different from other similar compounds prepared by Job and Baur. Analysis shows that the formula is $\text{Ce}_2\text{O}_4(\text{CO}_3)_{2.4}\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$.

The manner in which the oxygen is combined has been studied in considerable detail. It has been shown that two-thirds of the available oxygen is to be regarded as peroxide oxygen.

Two different methods for the determination of total available oxygen have led to the same conclusions. This work has confirmed Job's observation that the ordinary methods for the determination of total available oxygen are not applicable in such instances.

The preparation and properties of various other perceric derivatives will be given in another paper.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Victor Lenher for helpful suggestions and for the interest which he has at all times manifested in the above work.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE COLLEGE OF WASHINGTON.]

TWO METHODS OF SEPARATION OF THE METALS OF THE ALKALINE-EARTH GROUP.

BY ALICE G. PATERSON.

Received August 16, 1915.

Both methods are based on the slight differences in solubility of the relatively insoluble salts of the group, both being applications of the principle involved in fractional precipitation.

According to this principle, as is well known, if a precipitating agent, such as ammonium carbonate, is added to a solution containing a mixture of salts of metals whose carbonates are relatively insoluble, such as those of the alkaline earths, the least soluble carbonate is the one to be first precipitated. The carbonates continue to be precipitated in order of their solubility, with exceptional action only in the case of very high concentration. However, if barium, for instance, is precipitated as a carbonate, and then a solution of a sulfate is added, it is converted into the less soluble sulfate. Also, if barium is precipitated as a carbonate and a solution of a strontium salt is then added, barium carbonate dissolves, strontium carbonate being formed.

If, then, two or more precipitating agents are added to a solution containing a mixture of salts, any given metallic ion will unite with that acid ion which forms the least soluble salt.

This principle is employed by Stieglitz,¹ also by A. A. Noyes.² In the present instance the writer proposes its application to the group analysis.

The first method is as follows: the solution, containing salts of the alkaline-earth metals, is treated with excess of solutions of ammonium carbonate and ammonium sulfate together. Barium precipitates as sulfate, and calcium and strontium as carbonates. This mixture is brought to boiling and allowed to stand 20-30 minutes, with occasional stirring, as it has been found that the action is not immediately complete. Especially is this true in the presence of magnesium salts. Some magnesium may also be precipitated as magnesium ammonium carbonate. The mixture is then filtered, and the precipitate washed until free from precipitating agents. The precipitate is washed into a beaker, using as small an amount of water as possible, and 1.5 volumes of 1% acetic acid added, and the mixture brought to boiling, dissolving the carbonates and driving off carbon dioxide. Enough acid should, of course, be present to complete this action. The undissolved precipitate is barium sulfate. This is filtered off, using paper pulp; the precipitate is washed, and barium confirmed by the flame. The filtrate contains the acetates of calcium and strontium, possibly also some magnesium acetate. This filtrate is made slightly alkaline with ammonium hydroxide, is then treated with excess of ammonium carbonate and ammonium oxalate together, and the mixture is brought to the boiling point with stirring. It is then allowed to stand 20-30 minutes with stirring, is filtered, and the precipitate washed until free from precipitating agents. This precipitate consists of calcium oxalate and strontium carbonate. It is washed from the paper with a small amount of water, and 1.5 volumes of 1% acetic acid added, and the mixture stirred or shaken vigorously for a few minutes to dissolve the strontium carbonate and expel the carbon dioxide. As before, enough acid should be present to complete this action. It is then filtered, and the residue, consisting of calcium oxalate, washed. The filtrate is made slightly alkaline with ammonium hydroxide, and the strontium then precipitated with ammonium sulfate or ammonium carbonate, evaporating the solution if the volume is large, and confirmed with the flame, as is also the calcium in the calcium oxalate.

In the presence of both the carbonate and oxalate ion, the strontium is apparently nearly completely precipitated as carbonate, and the calcium as oxalate, provided a little time is allowed for the action to complete itself. In the absence of calcium, the entire precipitate formed upon the addition of ammonium carbonate and ammonium oxalate consists of the

¹ "Qualitative Chemical Analysis," II, p. 21, "Separation and Determination of Strontium."

² "Qualitative Chemical Analysis," p. 85.

carbonate of strontium, and dissolves easily in acetic acid. In the absence of strontium, the entire precipitate consists of the *oxalate* of calcium. This is only very slightly soluble in cold 1% acetic acid, so that in the absence of strontium, a very faint cloudiness results when the acetic acid solution is treated with ammonium carbonate. This solubility seems to decrease if the precipitate is allowed to stand the 20-30 minutes before filtering. A small amount of magnesium may appear here as magnesium oxalate, distinguishable from calcium by the flame.

The two most important points for a clear-cut separation are, first, the sufficient washing of the precipitates, and second, allowing the precipitates to stand before filtering. In this respect the method does not differ from others. If the washing is not thorough, and the sulfate remains in soluble form with the residue of insoluble sulfate and carbonate, it will, of course, combine with the strontium ion, when the strontium carbonate is dissolved by acetic acid, thus causing strontium sulfate to remain in the residue with barium sulfate. In regard to the second point, the time is probably necessary because the solubilities of certain of the salts are so nearly the same, as, for instance, that of barium sulfate and barium carbonate, and that of strontium sulfate and strontium carbonate; that time must be allowed for complete reversion to the less soluble of the two, although the action is nearly complete after simply heating the mixture. This seems to be indicated by the fact that when the precipitate of carbonates and sulfates was *not* so allowed to stand, before filtering, some barium appeared in the solution of acetates of strontium and calcium, even when the mixture was subsequently only warmed and not boiled with 1% acetic acid; also, that when the mixture *had* been allowed to stand, even bringing to a boil with 1% acetic acid showed no barium in the filtrate. This seems to be also true in the case of the strontium carbonate and calcium oxalate. If filtered at once, after the addition of the precipitating agents, or after a few minutes of warming, neither the calcium flame, when a small amount of calcium is used, nor the strontium, when a small amount of strontium is used, is pure. As the following experiments will show, this is not the case when the mixture of precipitates stands after being heated.

In the following experiments the mixture analyzed contained in every case 5 cc. of a normal solution of barium chloride, 5 cc. of a normal solution of calcium chloride, and 5 cc. of a normal solution of magnesium chloride, together with the amount of strontium salt specified. It was precipitated with 15 cc. ammonium sulfate solution (M), and 15 cc. ammonium carbonate solution (250 g. to the liter) and analyzed according to the foregoing outline. In every case enough water was first added to the solution to make the total volume 100 cc. No ammonium chloride was used. In the first five experiments following, the mixture was filtered

immediately after being heated with the precipitating agents. In the last two (6 and 7), the mixture stood 30 minutes before being filtered, and no barium appeared in the filtrate. Boiling with 1% acetic acid, after being thus allowed to stand, did not affect barium. Apparently a small amount of barium is present as barium carbonate, when precipitation is first effected. This is probably completely changed to barium sulfate on standing a short time.

- (1) 0.5 cc. 0.1 *N* SrCl₂ Mixed ppt. of carbonate and sulfate boiled with 5% HAc.
Distinct ppt. when tested for Sr with ammonium carbonate.
Indeterminate flame.
- (2) 0.7 cc. 0.1 *N* SrCl₂ Mixed ppt. of carbonate and sulfate boiled with 5% HAc.
Distinct ppt. when tested for Sr with ammonium carbonate.
Mixed flame.
- (3) 1 cc. 0.1 *N* SrCl₂ Mixed ppt. of carbonate and sulfate boiled with 1% HAc.
Distinct ppt. when tested for Sr with ammonium carbonate.
Ca and some Ba in flame.

The main barium sulfate residue, after being thoroughly washed, showed no calcium or strontium flame.

- (4) 1 cc. 0.1 *N* SrCl₂ Mixed ppt. of carbonate and sulfate boiled with 1% HAc.
Ammonium sulfate used to precipitate Sr. Slight ppt.
Barium flame with trace of strontium.
- (5) 1.5 cc. 0.1 *N* SrCl₂ Mixed ppt. of carbonate and sulfate warmed, not boiled with HAc.
Ammonium sulfate used to test for Sr.
Slight ppt. Sr and Ba flame.
- (6) 1.5 cc. 0.1 *N* SrCl₂ Stood 30 minutes after the addition of precipitating agents.
Mixed ppt. warmed, not boiled with 1% HAc. Ammonium sulfate used to test for Sr. No ppt., even on heating.

From Experiments 5 and 6 it would appear that if the mixed precipitate is allowed to stand before filtering, barium does not go into solution.

- (7) 2 cc. 0.1 *N* SrCl₂ Stood 30 minutes after the addition of precipitating agents.
Mixed ppt. boiled with 1% HAc.
Stood 20 minutes with ammonium carbonate and ammonium oxalate. Ammonium sulfate used to test for Sr. Slight ppt.
Solution evaporated and precipitated with ammonium carbonate. Considerable precipitate; fine, pure strontium flame. No barium.

2 cc. 0.1 *N* SrCl₂ = 8.7 mg. of strontium.

In the following experiments the mixture analyzed contained in every case, 5 cc. *N* barium chloride solution, 5 cc. *N* strontium chloride solution, 5 cc. *N* magnesium chloride solution, together with the amount of calcium salt specified. Total volume of solution made up to 100 cc. No ammonium chloride used. Procedure the same as in preceding experiments. In Expts. 1 and 2 the mixture of precipitated oxalate and carbonate was filtered immediately after being brought to boiling with the precipitating agents. In Expt. 3 this mixture was allowed to stand 20 minutes before filtering.

- (1) 1.5 cc. 0.1 N CaCl_2 5% HAc used for both separations.
Cloudy residue for calcium. Red flame, not free from strontium.
- (2) 2 cc. 0.1 N CaCl_2 1% HAc used for both separations.
Distinct residue for calcium. Mixed flame.
- (3) 2 cc. 0.1 N CaCl_2 1% HAc used for both separations. Stood 20 minutes with ammonium carbonate and ammonium oxalate before filtering.
Slight residue; fine calcium flame.
- 2 cc. 0.1 N CaCl_2 = 4 mg. of calcium.

In the following experiments the mixture analyzed contained, in every case, 5 cc. N calcium chloride solution, 5 cc. N strontium chloride solution, 5 cc. N magnesium chloride solution, together with the specified amount of barium chloride. Total volume 100 cc. Procedure the same as in the preceding experiments. In Expts. 1 and 2 the precipitate sulfate and carbonate was filtered immediately after being heated with the precipitating agents. In Expt. 3 this precipitate was allowed to stand 30 minutes after heating, before it was filtered.

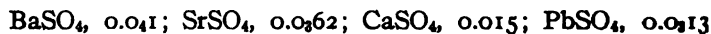
- (1) 0.5 cc. 0.1 N BaCl_2 Mixed ppt. of sulfate and carbonate boiled with 1% HAc .
Very slight residue. No flame test obtainable.
- (2) 1 cc. 0.1 N BaCl_2 Mixed ppt. of sulfate and carbonate boiled with 1% HAc .
Very slight residue. Barium flame.
- (3) 1 cc. 0.1 N BaCl_2 Mixed ppt. of sulfate and carbonate stood 30 minutes.
Boiled with 1% HAc . Considerable residue; strong barium flame.
- 1 cc. 0.1 N BaCl_2 = 6.8 mg. of barium.

Experiments 2 and 3 are the same, except for the difference of time. In 2 probably some of the barium remains as barium carbonate, dissolved in the acetic acid.

These amounts could be easily detected, giving decided residue and good flame tests.

The second method makes use of the same principle, with somewhat different application. In this method strontium sulfate is dissolved and the use of lead acetate, the less soluble lead sulfate being formed.

The solubilities (Stieglitz) of the sulfates of the alkaline-earth metals and of lead sulfate are as follows, given in mols per liter:



It will be seen that lead sulfate lies between barium sulfate and strontium sulfate. If lead acetate is added to a suspension of calcium sulfate, strontium sulfate and barium sulfate in water, calcium and strontium go into solution as acetates, lead sulfate being precipitated. Barium sulfate is not affected.

The method is as follows: A part of the solution is first tested for barium with potassium chromate and the flame. The remainder of the solution, without removing barium, is then treated with ammonium chloride.

and precipitation effected with ammonium sulfate, the mixture being brought to boiling. Most of the calcium remains in solution. Barium and strontium, with perhaps a small amount of calcium, are precipitated as sulfates. These are filtered off through paper pulp, washed twice, and then transferred by washing to a beaker and treated with an excess of lead acetate solution (*N*). This mixture is warmed, not boiled, for a few minutes and filtered. The filtrate contains strontium acetate, the excess of lead acetate, and probably a small amount of calcium acetate. The residue contains lead sulfate and barium sulfate. The filtrate is freed from excess of lead by hydrogen sulfide, and is then tested for strontium with ammonium sulfate, or with carbonate and oxalate according to Method 1.

It appears from the following experiments that if the mixture is boiled with lead acetate, some barium goes into solution. (Expts. 1 and 2.) If, however, the mixture of sulfates is warmed, but not boiled with lead acetate, barium does not dissolve, while strontium does. (Expts. 3 and 4.)

In every case the solution analyzed contained 5 cc. *N* barium chloride solution, 5 cc. *N* Ca solution, and 5 cc. *N* magnesium chloride solution together with the specified amount of strontium. Total volume 100 cc.

- | | |
|--|---|
| (1) 0.3 cc. 0.1 <i>N</i> SrCl ₂ | Precipitated sulfates boiled with lead acetate solution. Distinct cloudiness when testing for strontium with ammonium sulfate. Barium flame. |
| (2) No SrCl ₂ | Same as preceding experiment. Barium flame. |
| (3) No SrCl ₂ | Precipitated sulfates warmed but not boiled with lead acetate solution. No precipitate when tested with ammonium sulfate. Barium not dissolved. |
| (4) 1 cc. 0.1 <i>N</i> SrCl ₂ | Precipitated sulfates warmed but not boiled with lead acetate. Distinct cloudiness when tested for strontium with ammonium sulfate. Strontium separated by carbonate oxalate method. Gave fine, pure strontium flame. |
- 1 cc. 0.1 *N* SrCl₂ = 4.3 mg. of strontium.

The principle may have a wider application in general analytical work, and perhaps even possesses some value for quantitative separations. It may be seen that there are possibilities for very clear-cut and complete separations. The two methods as given work out rapidly and very satisfactorily. The writer has made use of the first method in the laboratory with students in the first semester of qualitative analysis, with very good results.

There arises the possibility of precipitating several metals by the use of two or more precipitating agents, and then by the addition of a soluble salt of a metal not under examination, dissolving one or more of those precipitated. Or, several salts having been precipitated by one reagent, a similar displacement being carried out. For instance, possibly the carbonate, oxalate, and sulfate could all be used together, to precipitate

barium, calcium, and strontium, these then being separated, first by the use of acetic acid, then dilute hydrochloric acid. Also, in precipitating calcium oxalate and strontium carbonate together, lead acetate may be used to dissolve calcium oxalate, leaving strontium carbonate, since the solubility of lead oxalate is less than that of calcium oxalate, but the solubility of lead carbonate is somewhat greater than that of strontium carbonate. The writer has not, however, carried out these separations. A large difference in solubility does not seem to be necessary; is not in fact desirable for the carrying out of such schemes.

A separation of copper and cadmium may be made by warming a suspension of the sulfides in water with lead nitrate solution. Cadmium sulfide dissolves; copper sulfide is not affected. The excess of lead is removed with ammonium sulfate, and cadmium precipitated as a sulfide. The objection to this method is that neither ammonium sulfate nor dilute sulfuric acid completely remove the lead, so that in testing for cadmium the solution is slightly discolored by lead sulfide. This, however, is not the case in the usual scheme of analysis, whenever lead is present.

The writer expects to continue work on this subject.

PULLMAN, WASHINGTON.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF GRINNELL COLLEGE.]

ACID POTASSIUM AND ACID SODIUM PHTHALATES AS STANDARDS IN ACIDIMETRY AND ALKALIMETRY.

By W. S. HENDRIXSON.

Received August 27, 1915.

Quite recently Francis E. Dodge¹ suggested acid potassium phthalate as a satisfactory standard in acidimetry and alkalimetry, and also suggested acid sodium phthalate as a possible standard, though having advantages over the potassium salt. His paper contains no analytical data, but is largely theoretical, and, so far as the writer has been able to learn, these substances have not been rigidly investigated with reference to their reliability for the purpose suggested. The two substances have certain properties, as pointed out by Dodge, that are very desirable in a standard, such as ease of preparation in the pure state, comparative ready solubility, and high molecular weights. It seemed to me a matter of interest to subject them to a careful experimental study in comparison with other standards of undoubted accuracy, to determine whether they can be relied on to give accurate results in standardization. To this end a solution of hydrochloric acid was made up by the method of Hulett and Bonner,² which should contain 0.003647 g. of hydrochloric acid per cc., and it was then further standardized by means of silver chloride, by two samples of benzoic acid, by acid potassium and acid sodium phthalates.

¹ *J. Eng. Ind. Chem.*, 7, 29 (1915).

² *THIS JOURNAL*, 31, 390 (1909).

Solution of Hydrochloric Acid.—Concentrated, chemically pure hydrochloric acid was distilled from a glass-stoppered distilling flask till three-fourths of it had passed over. Platinum scrap was used to prevent bumping. Without interrupting the distillation the condenser tube was then inserted into the neck of a bottle cooled in ice water and the process was continued till about three-fourths of the remaining one-fourth had distilled. The second distillate was at once used to make up the solution of 0.1 *N* HCl by the method of Hulett and Bonner.

The pressure being 740, according to Hulett and Bonner, 17.9745 g. of the distillate (air weight) should contain one-tenth mol of HCl. The amount of the acid weighed was 53.997 g. and it was made up to 3004.08 cc., measuring the solution at 20° by the content, not delivery, of three flasks previously calibrated by myself by actually weighing them filled with water to the mark at 20°. Introducing the necessary corrections for water weighed in air at that temperature with brass weights the three flasks were found to contain, when filled to their marks, 3.0004 liters. The additional volume of water was measured from a buret also calibrated for 20°.

In making up the hydrochloric acid solution, and at all other essential points, redistilled water was used. The boiler was of copper and it was fitted with a Kjeldahl distilling bulb to prevent the passage of spray. The condenser tube was of block tin and extended well into the receiving bottle. A seal of cotton between the tube and the neck of the bottle prevented currents of air. The collection of the water was begun only after about 500 cc. of water had passed over, so as to eliminate carbon dioxide. The water was kept stored in glass-stoppered, covered bottles till required.

The concentration of the hydrochloric acid solution thus prepared was determined by means of silver chloride, filtered and weighed in platinum Gooch crucibles in the usual manner. In all precipitation and washing about 1% of nitric acid was present. The filtrates were measured and usually amounted to about 500 cc., and 1.4 mg. of silver chloride was added to the weight for one liter of filtrate. The portions of the acid taken for precipitation were weighed.

In the early part of this work ordinary calibrated burets and flasks were used, but changing temperature, want of uniformity of drainage and the limit of volume in the case of burets to rather less than 50 cc. soon proved their inadequacy, and all results thus secured were rejected. In the determination of the hydrochloric acid and in all subsequent titrations weighing burets were used.¹ They weigh scarcely 50 g., hold

¹ They were made by the glass blower at the Chemical Laboratory, University of Illinois, at the instance of Professor W. A. Noyes, to whom I am greatly indebted. They are essentially the same as described by Washburn, *THIS JOURNAL*, 34, 1358 (1912) and used by him in his recent work on the value of the Faraday.

about 175 cc., and have long, slender delivery tubes to insert into other vessels, and very small tips so as to give small drops.

The following are the results of the determination of the concentration of the hydrochloric acid solution by means of silver:

	G. of soln. (air weight).	Wt. of AgCl.	HCl in 1 g. of soln.
1.....	64.215	0.9221	0.0036535
2.....	57.318	0.8232	0.0036541
3.....	63.945	0.9185	0.0036546
4.....	107.876	1.5489	0.0036532
5.....	99.748	1.4323	0.0036534

Average, 0.0036536

Since the concentrations of volumetric solutions are given commonly for 1 cc., this and all other values obtained per gram air weight should be calculated for 1 cc. To this end the density of the solution of hydrochloric acid was determined with a Sprengel picnometer by weighing the solution at 20° and comparing with the weight of water the instrument contained at the same temperature. The result was 1.0018. The density of water at 20 being 0.9982 and the product of these two values being almost exactly 1, it follows that the mass of 1 g. of the solution weighed in air is greater than 1 cc. only by the amount of the net buoyancy of air on 1 g. of water when weighed with brass weights. The buoyancy under the conditions is calculated to be 0.00107 gram. Therefore dividing the silver value 0.0036536 by 1.00107 the content of HCl in 1 cc. becomes 0.0036497. All subsequent values found for the HCl in 1 g. of the solution are calculated to 1 cc. in the same way.

Comparison of the HCl and an Alkali Solution.—Solutions of both barium and sodium hydroxides were made up, but the former seemed to have no advantage over the latter and had the disadvantage that the precipitates formed in titration interfered somewhat in judging the end points. It was soon discarded in favor of the sodium hydroxide.

Somewhat more than the required amount of sodium hydroxide (purified by alcohol) was weighed, sprayed with a little water to remove most of the superficial carbonate, and dissolved in about a liter of water. A slight excess of barium hydroxide was added to precipitate any carbonate and the excess of barium was removed by precipitation with a slight excess of sodium sulfate. The solution was filtered rapidly into a large bottle which had been filled with air free from carbon dioxide. Without exposing to the air till all the solution had run through, the filtration was stopped and enough pure water was added to the bottle to make the total volume about four liters. The bottle was fitted with a glass-stoppered buret which was filled through its side tube, also provided with a glass stopper. To prevent access of carbon dioxide the buret and bottle were provided with long calcium chloride tubes filled with bits of solid potassium

hydroxide. The guard tube connected with the bottle was in turn connected with a bottle containing a solution of concentrated caustic potash over which the air remained till drawn into the bottle containing the standard alkali in filling the buret. Over the tip of the buret was kept a rubber cap. The weight buret was filled from the volume buret, the tip of the latter being inserted far into the neck of the weight buret. A small constant amount of carbonate in the alkali, if present, would have mattered little, since in the series of titrations hydrochloric acid \leftarrow sodium hydroxide \rightarrow benzoic acid, for example, the influence of the carbonate would have been eliminated. For the same reason no correction was made for the error due to the fact that phenolphthalein, which was used as the indicator in all titrations shows the pink color only after the hydroxyl ions are slightly in excess.

All titrations were made in air free from carbon dioxide. A small Erlenmeyer flask was fitted with a thin section cut from a two-hole rubber stopper. One hole received the long delivery tube of the weight buret, and through the other was a tube reaching to the bottom of the flask, and connected with an apparatus to purify the air. The compressed air was contained in a large steel cylinder and passed from it to a large storage bottle with a layer a few centimeters deep of strong caustic potash. It then passed through three gas-washing bottles containing potash, through a similar bottle with water and finally to the titration flask.

In titrating the acid against the alkali both were weighed in weight burets, and the alkali was run into the hydrochloric acid. The air was allowed to run through the flask a short time before the addition of alkali was begun. This stream of air also served to agitate the liquid, obviating any need of shaking or stirring. Five closely agreeing titrations gave the ratio in grams of alkali to acid as 1 to 1.10991. A second solution of sodium hydroxide was prepared in the same way and its ratio to the acid was 1 to 1.1859. Which value applies in any given series of titrations will be indicated.

Standardizing with Benzoic Acid.—The benzoic acid used by Morey¹ in his investigation was fractionally sublimed *in vacuo*, which demands an amount of work and time that might seem excessive for ordinary purposes, student practice for example. It seemed desirable to make titrations of the best acid obtainable in the market after further purifying it by crystallization from alcohol and water and from water alone. The acid thus purified was melted in a platinum dish in an oven at 130°. The dish was placed in water and the cake of acid cracked loose. It was broken up and placed in a desiccator. In weighing the acid a platinum crucible was used, since it was less hygroscopic than glass. Weighed

¹ THIS JOURNAL, 34, 1027 (1912), Bureau of Standards, *Bull.* 8, p. 643.

portions were dissolved without heating in the titration flask in about 20 cc. of purified alcohol whose neutrality was tested. About an equal volume of pure water was added and the titration was carried out as already described, using as in all other instances phenolphthalein as indicator. The following are the results, the alkali having the ratio alkali to acid as 1 to 1.10991 being used:

	Wt. of NaOH.	Wt. benzoic acid.	Calcd. HCl in 1 g. of soln.
1.....	91.829	1.2470	0.0036559
2.....	82.139	1.1148	0.0036539
3.....	89.695	1.2169	0.0036525
4.....	79.778	1.0838	0.0036574
Av. of all titrations.....			0.0036549
The calculated amount of HCl in 1 cc. is, therefore.....			0.0036510

The calculated weight of HCl to 1 cc. is here found as described under standardization by means of silver chloride.

Another series of titrations was made using the special benzoic acid prepared by the Bureau of Standards for calorimetric and volumetric work. It was fused, weighed and titrated in the same way as the first sample, but the more concentrated alkali having the ratio to the hydrochloric acid 1 to 1.1859 was used.

	Wt. of NaOH.	Wt. benzoic acid.	Calcd. HCl to 1 g. of soln.
1.....	34.903	0.5062	0.0036544
2.....	54.767	0.7941	0.0036536
3.....	96.481	1.3990	0.0036536
4.....	139.791	2.0264	0.0036526
5.....	133.900	1.9410	0.0036525
Av. of all titrations.....			0.0036536
Calculating the HCl in 1 cc. as already described, the value is found to be			0.0036497

Standardization with Acid Potassium Phthalate, $\text{HKC}_8\text{H}_4\text{O}_4$.—The salt is anhydrous.¹ It is moderately soluble in cold water and its solubility is greatly increased by heat, and it can, therefore, be easily purified by crystallization from hot water. It was prepared by dissolving pure, sublimed phthalic anhydride and slightly more than the calculated weight of pure potassium carbonate to form the acid salt. This salt was purified by recrystallizing five times from hot water. Special purified water was used throughout, and a platinum vessel in the last crystallizations. After drying in air the sample was heated several hours at 125°, and its constancy of weight tested.

The following are the results obtained by titration of the first preparation

¹ Dodge, *Loc. cit.*

tion: The first three titrations were made with the alkali solution having the ratio by weight to the hydrochloric acid solution 1 to 1.10991. All the remaining titrations were made with the alkali having the ratio 1 to 1.1859.

Weighed portions of the acid salt were dissolved in about 50 cc. of water in the titration flask, which was kept loosely stoppered and usually was warmed slightly to hasten solution. Phenolphthalein was of course used as the indicator.

	Wt. of NaOH.	Wt. of $\text{HKC}_8\text{H}_4\text{O}_4$.	Calcd. HCl to 1 g. of soln.
1.....	64.275	1.4583	0.0036517
2.....	68.479	1.5531	0.0036503
3.....	96.585	2.1933	0.0036548
4.....	59.670	1.4483	0.0036565
5.....	49.471	1.2000	0.0036542

Av. wt. HCl in 1 g. of soln..... 0.0036535

The calculated value of HCl to 1 cc. of the solution is, therefore, 0.0036495.

The second preparation of the acid salt from which the following titrations were made was prepared from a new sample of the anhydride and special potassium carbonate made by repeated precipitation of the acid potassium carbonate from the normal carbonate with carbon dioxide. It was purified with the same or even greater care, as was used in the first preparation. The results of its titration are practically the same as in the first series.

	Wt. of NaOH.	Wt. of $\text{HKC}_8\text{H}_4\text{O}_4$.	Calcd. HCl in 1 g. of soln.
1.....	71.733	1.7380	0.0036500
2.....	56.660	1.3733	0.0036513
3.....	71.243	1.7287	0.0036554
4.....	78.108	1.8943	0.0036535
5.....	52.367	1.2692	0.0036512

Av. of all titrations..... 0.0036523

Calculating the weight of HCl to 1 cc. of the solution the result obtained is 0.0036484.

Standardization with Acid Sodium Phthalate, $\text{HNaC}_8\text{H}_4\text{O}_4$.—This salt has about the same solubility in hot and cold water as the potassium salt. It crystallizes with approximately one-half a molecule of water as determined by Dodge,¹ and the writer has confirmed his work both by titration of the salt and by loss on heating. Three preparations of this salt were made by the author with the same care described under the potassium salt. It was usually crystallized six times from hot water. Numerous titrations were made to determine whether

¹ *Loc. cit.*

the hydrous salt would give constant results but the figures were disappointing. The results thus obtained from the air-dried salt varied from about 1 part in 700 lower to about the same amount higher than corresponds to the formula $\text{HNaC}_8\text{H}_4\text{O}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. The hydrous salt when considered for titration purposes belongs to the same class, apparently, as oxalic acid and sodium tetroxalate. In the experience of the writer, however, it showed less variation from theory than the oxalates showed in the course of an extended and careful study of these under the same conditions. The study was made in the hope that oxalic acid and potassium tetroxalate might be used to compare with the acid phthalates as to their reliability, but so great was their variation from formula and want of constancy that the attempt had to be given up. In fact, determinations of the potassium in the potassium tetroxalate seemed to show definitely that this salt becomes more nearly neutral with repeated crystallization, and I hope to give this matter further study.

Much better results were obtained with dehydrated sodium phthalate. Before dehydrating the salt for use in titrations, it was subjected to certain tests to determine its stability when heated. A portion of the salt, contained in a porcelain boat, was heated in a tube through which passed a current of pure air, and this air was then passed through clear baryta water. It was gradually heated to 225° during an hour and held at that temperature an hour longer. No trace of carbon dioxide was indicated by the baryta water, but a very small amount of phthalic anhydride appeared in the cooler part of the tube after 200° had been reached. Since the salt can be completely dehydrated at 120° , no decomposition need be feared if reasonable care is taken. No such test of the stability of the potassium salt was made, since drying it is merely a matter of driving off hygroscopic water, and a temperature much above a hundred is not required.

The acid sodium phthalate used in the following titrations was dehydrated by heating at 120° . About 10 g. of it in a platinum dish attained constant weight in about three hours, but was heated longer in order to be perfectly sure of the constancy.

	Wt. of NaOH.	Wt. of $\text{HNaC}_8\text{H}_4\text{O}_4$.	Calcd. HCl to 1 g. of the salt.
1.....	42.754	0.9548	0.0036524
2.....	43.610	0.9737	0.0036515
3.....	52.897	1.1824	0.0036557
4.....	51.337	1.1470	0.0036540
5.....	61.626	1.3758	0.0036511
6.....	77.619	1.7354	0.0036565
7.....	51.479	1.1494	0.0036516
			0.0036533

The average for the seven experiments is 0.0036533 g. of HCl for 1 g. air weight of the HCl solution, which, as already explained, gives 0.0036494 g. HCl in 1 cc. of the solution.

To sum up the work we have the following values for the weight of HCl in 1 g. of the hydrochloric acid solution, prepared according to the method of Hulett and Bonner:

1. Constant boiling point, Hulett and Bonner.....	0.0036470
2. By means of silver chloride.....	0.0036497
3. By means of benzoic acid, first series.....	0.0036510
4. By means of benzoic acid, second series.....	0.0036497
5. By means of acid potassium phthalate, first series.....	0.0036495
6. By means of acid potassium phthalate, second series.....	0.0036484
7. By means of anhydrous acid sodium phthalate.....	0.0036494
<hr/>	
Average of all methods.....	0.0036492

There are, therefore, seven values based upon five standards and methods from which to determine the concentration of the solution of hydrochloric acid. The agreement is very close. The extreme difference is between the constant boiling-point method and the first series of titrations of benzoic acid. Even here the difference is 1 in more than 900 parts, which is yet within the limits of accuracy of ordinary titration in which the delivery of flasks and volume burets is used. The difference between the boiling-point method and the average of the titrations of benzoic acid is 1 part in more than 1100. It differs from the average of all results by 1 part in more than 1600, and its greatest difference from the results of any series where a phthalate was used is 1 part in 1460 too low. The experience of the writer is in close agreement with that of Morey¹ in whose work on benzoic acid as an acidimetric standard the method of Hulett and Bonner gave the concentration of the hydrochloric acid lower than any other standard, and by about the same amounts as just stated.

It may be observed that the results obtained by using silver, benzoic acid and the two acid phthalates as standards are almost identical. So far as the results go they indicate that one of the organic standards is as good as another in point of accuracy. The acid phthalates have some advantage in their much higher molecular weights, their greater solubility, and the fact that they can be prepared pure and true to the formulae accepted for the anhydrous salts without the use of unusual and time-consuming methods of purification. They may easily and quickly be prepared in large quantity for class use, and in fact their preparation may be considered easily within the powers of comparatively elementary students in volumetric analysis.

GRINNELL, IOWA,

¹ *Loc. cit.*

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

OXIDATION AND REDUCTION WITHOUT THE ADDITION OF ACID.**I. THE REACTION BETWEEN FERROUS SULFATE AND POTASSIUM DICHROMATE.**

BY MARKS NEIDLE AND JOSHUA C. WITT.

Received August 7, 1915.

The first use of the reaction between ferrous salts and dichromate for the determination of iron was made by Penny.¹ In the method, as described in his paper, a sample of "iron stone" was dissolved in hydrochloric acid, and the iron reduced by adding sodium sulfite in excess. After boiling off the excess sulfurous acid, he titrated with dichromate solution, using potassium ferricyanide as an outside indicator. It is interesting to note that this method is essentially the same as that in use today for the determination of iron in iron ore.

Whenever the reaction between ferrous salts and dichromate has been studied a mineral acid has been added. Penny employed excess of free acid in dissolving the iron ore, and the equation for the reaction demands free acid for the formation of the normal salts of potassium, chromium, and iron. Since no mention of any investigation of the reaction in the absence of free acid could be found in the literature, it was decided to perform a few preliminary experiments in which a quantity of ferrous sulfate was titrated by 0.1 *N* dichromate, with and without acid.

It was considered preferable to weigh out a separate portion of ferrous sulfate for each titration, rather than to keep a standard solution of the salt. As soon as a portion was weighed out it was rapidly transferred to a beaker containing water, and titrated at once with the dichromate solution, using potassium ferricyanide as an outside indicator. The following results were obtained showing the effect of acid:

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (g.).	Cc. $\text{K}_2\text{Cr}_2\text{O}_7$.	H_2SO_4 .
0.8	29.52	Excess present
0.8	29.54	Excess present
0.8	36.16	None present
0.8	36.25	None present

The end point is obtained when the amount of ferrous salt remaining at the time the drop test is made is insufficient to affect the indicator. When no acid is added, an excess of dichromate is required to give an end point, which means that with the theoretical amount of dichromate necessary to completely oxidize the ferrous sulfate, enough of the latter remains to affect the indicator, *i. e.*, the reaction is incomplete. A brown precipitate appears after a few drops of the dichromate have been added.

The following results show the effect of the volume of ferrous sulfate solution on the titration, 0.8 g. of salt being used in each experiment.

¹ *Brit. Assoc. Rep.*, [2] 1850, 58, 59.

Cc. water added to FeSO_4 .	Cc. dichromate sol. with H_2SO_4 .	Cc. dichromate sol. without H_2SO_4 .
0	29.67	29.89
5	29.88
15	30.03
30	30.62
100	32.12
1000	53.00

This increase in the dichromate was to be expected, since the reaction is slower the greater the volume, and larger amounts of dichromate are required to drive the reaction to the end point. When no water is added the result of the titration is nearer theoretical, and in several experiments, in which more than 0.8 g. was taken and the solid titrated, the result was exactly the theoretical. We may therefore conclude that the precipitate formed does not adsorb the ferrous ion appreciably. Adsorption of ferrous ion would vitiate the results on the velocity of the reaction.

Considerable difficulty was encountered in finding the end point at the higher concentrations when the titration was made in the absence of sulfuric acid. The brown precipitate had a tendency to mask the end point. To overcome this, when the end point was nearly reached, it was found necessary to filter a few drops of the mixture each time before it was applied to the indicator.

Measurement of the Velocity of the Reaction.—The problem which presented itself at this point was to find a method of determining the unoxidized ferrous salt or unreduced dichromate in a solution containing ferric salts, ferrous salts, chromic salts, and dichromate. Three methods suggested themselves:

(1) To stop the reaction by the addition of ammonium hydroxide, filter the precipitated hydroxides of iron and chromium, and determine the chromium in the precipitate.

(2) To add ammonium hydroxide as in (1) and titrate the unchanged dichromate in the filtrate.

(3) To precipitate the unchanged dichromate with lead acetate, dissolve the precipitate of the reaction in acetic acid, and determine chromate in the residue.

The second method, being more direct and therefore more accurate, was adopted.

It is well known that ferrous salts, in common with salts of other divalent metals, cannot be completely precipitated by ammonium hydroxide in the presence of ammonium salts in consequence of the repression of hydroxyl ion by the latter. In order to be certain of completely precipitating ferrous iron, the necessary conditions were investigated.

It was found that ferrous salts may be completely precipitated with ammonium hydroxide provided,

- (1) The solution is neutral.
- (2) No ammonium salts are present to begin with.
- (3) The concentration is sufficiently low.
- (4) The solution is boiled and the precipitate allowed to settle before filtration is attempted.

If 0.5 g. portions of ferrous sulfate were dissolved in various volumes of water, and an excess of ammonium hydroxide added, the precipitation was complete only when the volume was at least 100 cc.

Solutions.

Potassium Dichromate.—A 0.1 *N* solution, standardized against iron wire, was kept in a ten-liter bottle fitted with a siphon. All air entering the bottle came through a cotton plug to avoid contamination.

Sodium Thiosulfate.—A 0.01 *N* solution was standardized each time before using against the dichromate solution.

Ferrous Sulfate.—At first it was thought advisable to make up a standard solution of ferrous sulfate and attempt to protect it from oxidation, but it was finally decided to use the dry salt and weigh out a portion for each determination. To avoid difficulty from any variation in quality, a fresh pound bottle of the c. p. salt was taken, and used for all the work. The surface layer was discarded, a weighing bottle filled and kept in the balance until used, then refilled when necessary. In weighing out a sample, a slight excess was placed on the balance and the stopper of the weighing bottle replaced at once. The excess salt was removed as quickly as possible and discarded to avoid any possible contamination. The salt was analyzed from time to time and found to remain constant in composition, as shown by the following results obtained with 0.8 g. samples:

Date.....	April 5.	May 3.	June 9.
Titration with 0.1014 <i>N</i> $K_2Cr_2O_7$	29.53 cc.	29.67 cc.	29.63 cc.

Manipulation.—A large, electrically controlled bath was maintained at $30^\circ \pm 0.05^\circ$. A ten-liter bottle of distilled water was kept in this bath that no delay might be caused by waiting for water to assume the correct temperature.

Nearly as much water as was needed for the experiment was placed in a liter flask corrected for temperature, and a given amount of standard dichromate solution was run into an Erlenmeyer flask. Both flasks were immersed in the bath and allowed to assume constant temperature. In the meantime a portion of the ferrous sulfate was weighed and rapidly transferred to the liter flask. When solution was complete, the dichromate was added and the volume adjusted. The flask was kept in the bath and, at intervals, 100 cc. portions were removed and run into beakers containing excess of ammonium hydroxide.

The precipitate formed by the ammonium hydroxide was very finely divided and would pass very readily through the filter. It was

found necessary to let it stand some time—preferably over night—or to boil it a few minutes before a complete filtration could be made. It was preferable to filter at once, without heating, but no method could be found which gave the desired result. The precipitate passed through an alundum Gooch, and would not settle when kept in a centrifuge for 15–20 minutes.

In order to determine whether the potassium dichromate still in solution was in any way affected by the precipitated ferrous iron, 25 cc. of 0.1 *N* dichromate was added to 0.8 g. of ferrous sulfate dissolved in water in a liter flask, and, after introducing an excess of ammonium hydroxide, the mixture was made up to volume. A number of 100 cc. portions were withdrawn and placed in beakers. They were filtered at various intervals and titrated with 0.01 *N* thiosulfate by the method already described. Some were boiled before filtering, and others were filtered in the cold. The following are the results obtained:

Time.	Titration, 0.01 <i>N</i> thiosulfate.	Remarks.
2 hours	0.90 cc.	Not boiled
2 hours	1.00	Boiled
24 hours	0.94	Not boiled
24 hours	1.00	Boiled

It is seen from the above that the final result is not altered by allowing the mixture to stand for many hours, or by boiling, before filtration.

Results.—All measurements were made at 30°. The ferrous sulfate and dichromate solution were in the ratio of 0.8 g. of the former to 25 cc. of the latter, or 2.878 mols to 0.4225 mol. It was not thought advisable to attempt any measurements with more dichromate than would be required for the normal end point, since in this case a very large volume of 0.01 *N* thiosulfate would be required. The ratio of the reacting substances was maintained constant. The volume of dichromate reduced is represented by x and that unreduced by $a - x$.

TABLE I.

Total Volume Containing 25 cc. of 0.1014 *N* $K_2Cr_2O_7$ and 0.8 g. $FeSO_4$.

Min- utes.	100 cc.		250 cc.		500 cc.		1,000 cc.		2,000 cc.		4,000 cc.		5,000 cc.	
	$a - x$.	x .	$a - x$.	x .	$a - x$.	x .	$a - x$.	x .	$a - x$.	x .	$a - x$.	x .	$a - x$.	x .
1	0.06	24.94	0.22	24.78	0.35	24.65	1.50	23.50	1.93	23.07
5	0.03	24.97	0.18	24.82	0.34	24.66	1.46	23.50	1.99	23.01	2.69	23.31
15	0.04	24.96	0.23	24.77	0.30	24.70	0.93	24.07	1.74	23.26	1.65	23.35	2.20	23.80
30	0.04	24.96	0.22	24.78	0.29	24.71	0.80	24.20	1.36	23.64	1.57	23.43	2.20	23.80
60	0.04	24.96	0.19	24.81	0.26	24.74	0.61	24.37	1.06	23.94	2.31	23.69

One series of experiments was made with method number three as a check. The work was carried on in the same way up to the time when 100 cc. portions were removed from the liter flask. In this case they were run into beakers containing lead acetate solution, which precipitated the

sulfate ion and the chromate ion. The mixture was then acidified with a few cubic centimeters of acetic acid and boiled to dissolve all the iron salts. The lead salts were then filtered out and the lead chromate dissolved in dilute hydrochloric acid. The resulting dichromate was titrated, after cooling, with 0.01 *N* thiosulfate. The results given in Table II compare satisfactorily with those previously obtained and given in Table I.

TABLE II.

Minutes.	$a - x.$	
	Method III.	Method II.
5	1.49	1.46
15	0.98	0.93
60	0.59	0.61

Comments on Velocity Measurements and the Order of the Reaction.

From Table I it is seen that in the titration of 0.8 g. of ferrous sulfate with dichromate, the reaction is 99.8% complete at the end of one minute, provided the final volume is 100 cc. This statement may be made even though in our experiments the dichromate taken was a little less than equivalent to the ferrous sulfate. At all other concentrations except the most dilute, the reaction is more than 90% complete at the end of the first minute.

The data as obtained are not of a nature to permit ready calculation of the order of the reaction, although those in the last column of Table I seemed sufficiently regular to justify an attempt at such a calculation. No constant could be obtained by assuming the reaction to be of the first order with respect to each of the reacting substances, of the first order with respect to one and of the second with respect to the other, and, finally, of the second order with respect to both. Our conclusion, therefore, is that this reaction is probably of an order higher than the fourth.

The rate of oxidation of ferrous sulfate by dichromate with the addition of more than the sulfuric acid required by the normal equation has been investigated by Benson.¹ It is stated in his conclusions that the rate is proportional to the second power of the concentration of ferrous salt, and to the second power of that of the acid, and that the order is variable with respect to the dichromate. Benson also found that the order is much retarded by the presence of ferric salts. If the velocity of this reaction is strictly proportional to the square, or any other power, of the concentration of acid added it should be zero when no acid is employed.

There can be no question, however, that the velocity is proportional to some power of the hydrogen-ion concentration, in which case the velocity of the reaction without the addition of acid is due to the hydrogen-ion concentration arising from the hydrolytic dissociation of both dichromate and ferrous salt. The concentration of hydrogen ion must play an

¹ *J. Phys. Chem.*, 1, 1 (1903).

important part in the reaction, even in very low concentration. Our reaction is most probably accompanied by a change in the concentration of hydrogen ion, which was disregarded in our velocity calculations. For this reason, we can not conclude with certainty that the reaction is of an order higher than the fourth.

The great velocity of the reaction without the addition of acid is partly due to the fact that less than one-third of the iron remains in solution as ferric salt, which has a retarding influence, while the remainder precipitates in the form of hydrous ferric oxide and adsorbed ferric sulfate.

The Products of the Reaction.—Preliminary experiments showed that all the brown precipitate, ultimately formed when solutions of dichromate and ferrous sulfate are mixed, does not come down instantly, but gradually, reminding one of the precipitation of suspensoids by small quantities of electrolytes. Upon filtering the mixture after it had stood for several days, the filtrate still yielded apparently the same precipitate on standing. The precipitation, it was found, could be rendered complete by boiling, when a reddish brown, gelatinous precipitate, resembling ferric hydroxide, appeared.

One-tenth of the equivalent weights of potassium dichromate and ferrous sulfate were dissolved in water and the solutions mixed, diluted nearly to a liter and heated to boiling for several minutes to bring about complete precipitation. After cooling, the mixture was made up to a liter exactly. The precipitate was brown and very abundant. The supernatant liquid had the purplish green color characteristic of chromium salts.

It was thought that heating the mixture might have some effect on the reaction. To settle this point, another solution was made up exactly like the one already described, except that it was not heated. After standing over night, it was filtered and both precipitate and filtrate were analyzed along with those of the first mixture, giving practically the same results. Although the precipitation was not complete, the difference was practically negligible. The work on this second solution was dropped, therefore, and only the first carried on.

The brown precipitate from the first mixture was dried to constant weight at $100-105^{\circ}$, giving a very hygroscopic amorphous powder. This solid and also the filtrate were analyzed for SO_3 , Cr_2O_3 , and Fe_2O_3 .

The SO_3 was determined as BaSO_4 . To determine iron and chromium, the hydrochloric acid solution was neutralized with sodium hydroxide and the chromium oxidized by sodium peroxide. After boiling, the ferric hydroxide was filtered out and washed with hot water. The precipitate was then dissolved in hot hydrochloric acid, reprecipitated with sodium hydroxide, again treated with sodium peroxide, filtered and washed. The two filtrates were combined, boiled, acidified with hydrochloric acid (5 cc. in excess) and again boiled for some time. After cooling, 10 cc. of

a 10% potassium iodide solution was added, and the solution titrated with 0.1 *N* thiosulfate, using starch as the indicator.

The iron was again dissolved, brought nearly to dryness on the hot plate, reduced by stannous chloride and titrated with 0.1 *N* potassium permanganate.

FILTRATE.			
	Grams.	Gram equivalents.	Percentage of total in precipitate.
SO ₃	6.241	0.1560	8.006
Fe.....	1.176	0.0631	5.590
Cr.....	1.122	0.0647	1.733
			35.26

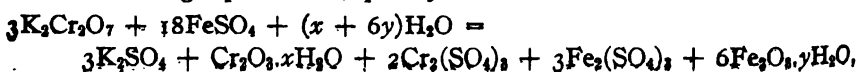
PRECIPITATE.			
	Grams.	Gram equivalents.	Percentage.
Fe ₂ O ₃	6.313	0.2369	56.03
Cr ₂ O ₃	0.894	0.0353	7.93
SO ₃	1.755	0.0440	15.58
Loss on ignition (except SO ₃).....	2.239	19.87
Undetermined (K ₂ O).....	0.067	0.0015	0.59

Further Investigation of the Precipitate.—It is seen that the precipitate contains quantities of all the salts produced in the reaction. In order to ascertain the nature of these adsorbed salts, a weighed portion of the precipitate was boiled in water for some minutes, and filtered. The filtrate was made up to 250 cc., and 25 cc. portions removed for analysis. It was found that the filtrate contained 2.11% SO₃, calculated on the basis of the amount of precipitate taken; or, 13.54% of the SO₃ present in the original precipitate had been removed by the first boiling.

A 50 cc. portion of the filtrate, analyzed for iron, gave 0.69%, approximately the amount required to correspond to the formula Fe₂(SO₄)₃. We may therefore conclude that the adsorbed salt is mainly Fe₂(SO₄)₃.

Discussion of Results on the Products of the Reaction.—The value 35.26% for the amount of chromium in the precipitate suggests that one-third of the total is precipitated as Cr₂O₃ and the remaining 1.93% adsorbed as Cr₂(SO₄)₃. If we add the number of equivalents corresponding to the adsorbed potassium sulfate and chromium sulfate, and subtract the sum from the total number of equivalents of SO₃ in the precipitate, the result gives the number of equivalents of Fe₂(SO₄)₃ adsorbed. This value is 0.0407, which, added to the number of equivalents of Fe₂(SO₄)₃ in the filtrate (0.0631), gives the number of equivalents of this salt formed in the reaction (0.1038). The mixture contained sufficient iron for 0.3 equivalents of Fe₂(SO₄)₃. Thus two-thirds of the iron forms hydrous ferric oxide, and one-third forms ferric sulfate.

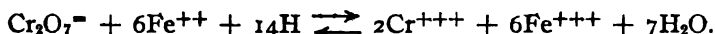
The following equation completely harmonizes with the above results:



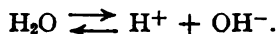
where $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot y\text{H}_2\text{O}$ stand for the colloidal oxides of chromium and iron, each carrying adsorbed water.

The products of the reaction between potassium dichromate and ferrous sulfate without the addition of acid are: potassium sulfate, chromium sulfate and colloidal chromic oxide in the molar ratio of 2:1; and ferric sulfate and colloidal ferric oxide in the molar ratio of 1:2. The colloids are precipitated by the sulfate ion in the solution.

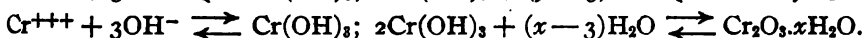
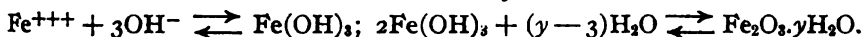
The normal ionic reaction is written



We believe that the reaction without acid proceeds in the same way, the hydrogen ion being derived from the water.



As hydrogen ion is consumed by the reaction, more is formed, and at the same time hydroxyl ion accumulates. Soon the concentration of hydroxyl ion is sufficient to exceed the solubility products of the hydroxides of iron and chromium, and the colloidal hydrous oxides are formed.



The manner of the precipitation of the oxides led us to the belief that they were formed in the colloidal state in the reaction. Chloride ion is a far less powerful precipitant for positive colloids than sulfate ion. Hence in the reaction between ferrous chloride and potassium dichromate we may expect that the colloids will not be precipitated and, on dialysis, it should be possible to isolate a mixed hydrosol of chromium and ferric oxides. Such is actually the case. Work on this reaction is now in progress and the results will be duly reported.

The investigation of the reaction between stannous chloride and potassium dichromate has been completed and will be the subject of the second article of this series.

Summary.

1. The stoichiometric relations in the reaction between potassium dichromate and ferrous sulfate are the same with or without acid.
2. The experimental conditions for the complete precipitation of ferrous iron by ammonium hydroxide have been found and employed to determine dichromate in a mixture also containing ferrous, ferric, and chromium salts.
3. Without acid the reaction is instantaneous, except in very dilute solutions.
4. Disregarding the change of hydrogen-ion concentration accompanying the reaction, the order is higher than the fourth.
5. The rate of the reaction, with acid, can not be proportional to the second power of the concentration of acid added, for then it should be zero without acid.

6. The products of the reaction are the sulfates of potassium, chromium, and iron, and the colloidal hydrous oxides of iron and chromium. The latter are precipitated by the sulfate ion, and adsorb a large quantity of ferric sulfate and smaller quantities of the other two sulfates.

7. The equations for the reaction have been formulated.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

BY HARRY SHIPLEY FRY.

Received June 17, 1915.

A paper recently published by Roger F. Brunel,¹ presents some general and some specific criticisms of the electronic conception of valence. The author states that the object of his paper² "is to call attention to certain weaknesses in the arguments put forward in support of this conception and certain difficulties that arise in applying it to chemical phenomena."

Brunel then subjects to criticism, either directly or indirectly, the opinions of a number of authors who have contributed to this subject. None of Brunel's specific criticisms have any bearing upon the applications in which I am principally interested, namely the problem of substitution in the benzene nucleus³ and the development of relationships between chemical constitution and absorption spectra.⁴ But, on the other hand, some of his general criticisms call for comment, especially certain statements presented in a paragraph on page 718.⁵ In quoting this paragraph, the assertions which it embodies have been numbered 1, 2, and 3 for facility in comment. Brunel states:

"Of the other applications of the theory to the more complex problems the author [Brunel] would mention only that of Fry to the question of substitution in the benzene ring. (1) The rule governing the positions of substituents which Fry puts forward with the utmost confidence is so simple as to arouse distrust at once. (2) It would appear sufficient to say that, in view of the extensive investigations carried on in this field in recent years by Holleman, Flürscheim, Obermüller and others, if any such rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms. (3) Holleman

¹ THIS JOURNAL, 37, 709 (1915).

² *Loc. cit.*, p. 710.

³ Fry, THIS JOURNAL, 30, 34 (1908); *Z. physik. Chem.*, 76, 385 (1911); THIS JOURNAL, 34, 664 (1912); *Ibid.*, 36, 243, 262, 1035 (1914); *Ibid.*, 37, 855, 863, 883 (1915).

⁴ Fry, *Z. physik. Chem.*, 76, 398, 591 (1911); *Ibid.*, 80, 29 (1912); *Ibid.*, 82, 665 (1913).

⁵ *Loc. cit.*

has, however, recently called attention to a number of cases of substitution where it is quite impossible to apply Fry's rule."

This paragraph can not be regarded as fulfilling in any sense the above noted purpose of Brunel's paper. Furthermore, it embodies assertions (1, 2, and 3) which call for comment. (1) Brunel's statement that Fry's rule "*is so simple as to arouse distrust at once*" is purely arbitrary because it has no bearing whatever upon the numerous and extended applications of the rule published by Fry.

Consider briefly Brunel's assertion (2):

"It would appear sufficient to say that in view of the extensive investigations carried on in this field in recent years by Holleman, Flürscheim, Obermüller and others, if any such simple rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms."

In this statement Brunel not only imposes a limitation upon the possibility of the discovery of new rules and relationships but he also completely ignores the well-known fact that the Brown and Gibson Rule is itself a purely empirical rule for determining whether a given mono-substituted derivative of benzene will yield chiefly a mixture of ortho and para diderivatives, or chiefly the meta diderivative. Moreover, Fry's rule is the direct result of his interpretation of the empirical Brown and Gibson rule in terms of the electronic conception of positive and negative valences in conjunction with his electronic formula for benzene.

Consider next Brunel's assertion (3):

"Holleman¹ has, however, recently called attention to a number of cases of substitution reactions where it is quite impossible to apply Fry's rule." This assertion can not be accepted as final, since Fry² has published "A Reply to A. F. Holleman" showing that Holleman's inability to correlate Fry's rule with certain cases of substitution was due to Holleman's failure to apply to the principle of the electronic tautomerism of benzene derivatives the generally accepted principle that, in a tautomeric equilibrium mixture, either one, or the other, or both tautomers (depending upon conditions), may interact with a given reagent. Thus from the standpoint of the electronic tautomerism of benzene derivatives, the simultaneous formation of ortho, para, and meta substituted derivatives was readily explained.³ Furthermore, those cases of substitution which Holleman regarded as opposed to Fry's rule were shown to conform to the rule and to serve as direct experimental evidence substantiating the principle of the electronic tautomerism⁴ of benzene derivatives.

¹ THIS JOURNAL, 36, 2495 (1914).

² *Ibid.*, 37, 883 (1915).

³ Fry, *Ibid.*, 37, 863 (1915).

⁴ Brunel objects to the use of the conception of electronic tautomerism on the grounds that electronic isomers (electromers) have not as yet been isolated. This ob-

Passing from the foregoing assertions, it will be found that some of Brunel's general conclusions also invite comment. Consider the statement on page 721:¹

"In conclusion the author would call attention to the fact that the 'electron conception of valence' cannot avoid dealing with the question of chemical affinity, *i. e.*, the attractive force between atoms."

To this it may be replied, and justly maintained, that *the electronic conception of valence as a formulative hypothesis* (*i. e.*, the conception of positive and negative valences as applied to structural formulas) is, at its present status of development, neither primarily nor necessarily concerned with the question of the ultimate cause of chemical affinity. Such questions inevitably lead into a field where speculation predominates. An illustration of this is afforded by the recent and varied hypotheses of J. J. Thomson which manifest little, if any, discernable *utility* in the interpretation of the mechanism of chemical reactions and the correlation of the various phenomena of Organic Chemistry.

Brunel closes his paper with this statement:

"A number of questions are proposed which should be answered—at least, the hypotheses regarding them should be explicitly stated—before the theory is applied to the most perplexing problems of organic chemistry." In reply, *the hypothesis of positive and negative valences has been explicitly stated*. A careful study of most of the published applications of the hypothesis shows that it is used primarily to qualify, or to differentiate, the valences of an atom as positive or negative in the same manner that we may regard a positive hydrogen ion as a hydrogen atom possessing a positive valence; or a negative chlorine ion as an atom possessing a negative valence. In applying these conceptions we are entitled to assume, *symbolically* at least, that an atom with zero valence develops a unit positive valence through the loss of an electron. Another atom with zero valence develops a unit negative valence through the acquisition of an electron. From this point of view I have suggested a general rule² for applying the conception of positive and negative valences to various atoms, namely that if the valence of an atom equals (*n*) in the ordinary meaning of the term, then that atom, from the standpoint of the con-
jection is unwarranted because the use of the conception of tautomerism neither involves nor demands the immediate possibility of the isolation of the tautomers. Strictly speaking, the term *tautomeric* is applied to substances in which *only the equilibrium mixture of the structural isomers is known*; the term *desmotropic* is employed in cases where *the isomers have been shown to be capable of independent existence*. (Experiments are now in progress in this laboratory, the object of which is to establish the independent existence of "*electronic desmotropes*.")

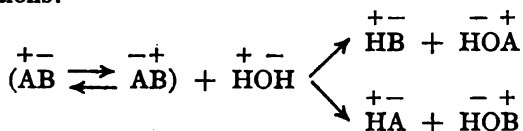
¹ *Loc. cit.*

² Fry, *THIS JOURNAL*, 30, 34 (1908); *Z. physik. Chem.*, 76, 388 (1911).

ception of positive and negative valences, may function in $(n + 1)$ different ways.¹

Furthermore, the development of a positive valence by an atom (*schematically* through the loss of an electron) corresponds to oxidation. When an atom develops a negative valence (*schematically* through the acquisition of an electron) it is reduced. *The extensive field of oxidation and reduction reactions thus affords an experimental justification for the use of the electronic conception of positive and negative valences.* This phase of the hypothesis also possesses an added significance, since Stieglitz² has demonstrated by means of the chemometer that there is involved an actual transfer of electrical charges in certain oxidation and reduction reactions involving carbon compounds.

Again, if we admit that the hydrogen ion is positive and, that the hydroxyl ion is negative under normal conditions, *i. e.*, provided that the hydrogen ion is not reduced and that the hydroxyl ion is not oxidized, then it is natural to conclude that *hydrolysis reactions constitute an experimental method for designating the polarity of the radicals of a compound under the particular conditions of the hydrolysis.* The following general scheme (in contradistinction to the scheme presented by Brunel on page 718,³ embodies the theoretical and the actual possibilities presented by hydrolysis reactions:



If the compound AB on hydrolysis yields only HB and HOA, then AB is *qualified* by the formula $\begin{array}{c} + - \\ AB \end{array}$. If, on the other hand, conditions are such that the products of hydrolysis are HA and HOB, then AB is *qualified* by the formula $\begin{array}{c} - + \\ AB \end{array}$.

In some reactions four products of hydrolysis are obtained, and accordingly, the compound AB presents an illustration of electronic tautomerism,⁴ *i. e.*, the existence of both electromers $\begin{array}{c} + - \\ (AB \rightleftharpoons AB) \end{array}$ in dynamic equilibrium. Many instances⁵ have been recorded in which reactions proceed according to the above and analogous schemes, and therefore substantiate not only the existence of electromers but also electronic tautomerism. Hence, *as a corollary to the experimental*

¹ This rule has been repeatedly illustrated in various papers by Fry (*Loc. cit.*). Its application to the valences of the nitrogen atom and its various compounds has been presented in detail by L. W. Jones, *Am. Chem. J.*, 50, 414 (1913).

² *Qual. Chem. Anal.*, 1, Chaps. XIV and XV (1911).

³ *Loc. cit.*

⁴ Fry, *Z. physik. Chem.*, 76, 390 (1911).

⁵ Fry, *THIS JOURNAL*, 37, 864 (1915).

facts, it seems justifiable to maintain that the ordinary structural formula for AB, namely $A-B$, is qualified when it is written $A \overset{+}{-} B$, or $A \overset{-}{+} B$, or both ($A \overset{+}{-} B \rightleftharpoons A \overset{-}{+} B$), depending upon the conditions of the experiments and the products obtained. Therefore, *in designating the ends of a bond as positive or negative, one is not concerned primarily or necessarily with the question of the nature of chemical affinity* (a point upon which Brunel has insisted). The chief value and claim for recognition of electronic formulas (and for the existence of electronic tautomers in dynamic equilibrium) should and does lie in the fact that *in numerous instances they are more precise and more significant in the explanation of chemical phenomena and the mechanism of reactions than are the ordinary structural or graphic formulas.*

In conclusion, consider briefly a significant statement made in 1867 by Kekulé which illustrates the principle at issue:

"The question whether atoms exist or not has but little significance from a chemical point of view: its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. More especially have we to consider the question whether a further development of the atomic hypothesis promises to advance the knowledge of the mechanism of chemical reactions."

Kekulé's efforts to develop a knowledge of the mechanism of chemical reactions are today embodied in the structure theory, the recognized foundation of the extensive achievements of organic chemistry, both theoretical and applied. The established utility of *the structure theory* (which in reality is a *formulative hypothesis*) is not dependent upon the existence of atoms nor upon the fundamental nature of valence or chemical affinity. Similarly, the utility of *the electronic conception of positive and negative valences* (which is also a *formulative hypothesis* with the structure theory as its foundation), is not primarily dependent upon the existence of electrons nor upon the fundamental nature of chemical affinity. The significance of this viewpoint may become more evident if the words of Kekulé (quoted above) be paraphrased in modern terms: In chemistry we have to decide whether the electronic conception of positive and negative valences is an hypothesis adapted to the explanation of chemical (and physical) phenomena. More especially have we to determine whether the further development of this hypothesis of positive and negative valences promises to advance our knowledge of the mechanism of chemical reactions. In view of the fact that electronic formulas, in many instances, have proven to be more precise and more significant than the ordinary structural formulas in the explanation of chemical phenomena and the mechanisms of reactions,

the hypothesis of positive and negative valences may possibly become a necessary adjunct to the structure theory. This, as I have stated before,¹ must depend upon the extent of its applications and experimental verifications, and upon the part that is played by just criticisms in bringing to light the relative merits and demerits of its *applications*.

From these and the preceding points of view noted in this paper, the general criticisms and conclusions of Brunel have little, if any, bearing upon the *electronic conception of positive and negative valences as a formulative hypothesis*.

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[FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK, AND THE CHEMICAL DEPARTMENT, GOUCHER COLLEGE, BALTIMORE, MD.]

NEPHELOMETRIC ESTIMATION OF PHOSPHORUS.

BY PHILIP ADOLPH KOBER AND GRETE KOBER.

Received May 28, 1915.

TABLE OF CONTENTS.—I. Introduction. II. Reagent. III. Discussion. IV. Applications. V. Summary.

I. Introduction.

The estimation of phosphorus in biological and industrial sciences, especially of minute amounts, is becoming of increasing importance. A large number of volumetric and colorimetric methods have been proposed but thus far none has been satisfactory for micro-quantitative work. While looking for a suitable nephelometric precipitant² for phosphorus in connection with our nuclease technic³ our attention was called⁴ to the reagent developed by Pouget and Chouchak.⁵ This reagent consists of a nitric acid solution of strychnine and molybdic acid and produces a very sensitive reaction with phosphates (one milligram of phosphorus in 2 liters giving a very marked suspension of insoluble substance) similar in sensitiveness to the Nessler or the Graves⁶ reaction for ammonia. The authors found it will detect 1 part of phosphorus in 20 million parts

¹ THIS JOURNAL, 37, 892 (1915).

² Uranium acetate and magnesia mixture were tried as nephelometric precipitants, but as preliminary experiments, especially with the latter, were not successful, these reagents were abandoned.

³ P. A. Kober and S. S. Graves, THIS JOURNAL, 36, 1304 (1914).

⁴ Dr. I. Greenwald of this laboratory, after making an attempt to apply this reagent directly for nephelometric work, abandoned it. Subsequently (see *J. Biol. Chem.*, 21, 29 (1915)) he recommended the original reagent for a colorimeter method, although, according to him, the color of the opalescent liquid is so slight that it is not apparent until it is put into the instrument. It is obvious that any defect in the suspension for nephelometric work will make a defect for colorimetric, and our experiments, as indicated elsewhere, show that the reagent as recommended by the original authors, although usable, is not satisfactory.

⁵ *Bull. soc. chim.*, 5, 104 (1909); 9, 649 (1911).

⁶ THIS JOURNAL, 37, 1181 (1915).

of water. As the precipitate is slightly yellow and remains in suspension for a long time, the authors recommended it as a colorimetric reagent, but, practically, their estimations were turbidimetric.

On studying the reaction carefully, we found that (1) it was not constant and quantitative¹ and (2) the reagent gradually become yellow and deteriorated, probably because of the action of the nitric acid. Pouget and Chou-chak realized this, as their directions state that the mixing of constituents must be made only just before using. After making many variations of all constituents, no marked improvement was obtained, but *on substituting hydrochloric for nitric acid, the solution not only remained practically colorless for an indefinite length of time, but was stable and gave quantitative and constant results.*

II. Reagent.

(a) **Variations of Constituents.**—The insoluble substance formed in this reaction is probably a phosphomolybdic acid complex of strychnine. The important factor is the hydrochloric acid content of the reagent. If the amount of acid is too small, an insoluble strychnine-molybdic acid compound precipitates and if too large, the phosphate precipitate is redissolved. The latitude between these extremes is, however, quite satisfactory. Owing to the insolubility of the molybdic acid complex of strychnine, no large variations of strychnine could be made and therefore the solution used was saturated with respect to strychnine.

The amount of hydrochloric acid necessary for the reagent, using commercial grades of molybdic acid or sodium molybdate, was very difficult to determine, for the reason that some grades of molybdic acid obtained contained as much as 11% of ammonia; a few samples of sodium molybdate were soluble in water, and others were not. Merck's² sodium molybdate was found satisfactory, but difficult to obtain, so that the preparation of this substance by ourselves was necessary.

To show the effect of varying amounts of strychnine and hydrochloric acid, the following experiments were made:

Strychnine.—To 1.5 g. of sodium molybdate, dissolved in 2.5 to 3.25 cc. of water, and 10 cc. of hydrochloric acid (1-1) sp. gr. 1.098, were added 1.0, 0.75, 0.50, 0.25 and 0.00 cc. of a saturated solution of strychnine sulfate (2%), respectively.

After shaking and standing over night, molybdic acid-strychnine crystallized out in all solutions, except the last. The one to which 0.25 cc. of strychnine sulfate had been added contained the least (only a small amount), while the others contained precipitates in proportion. The reagents were, after filtering, tested for their precipitating power nephelometrically, and it was found that the one without strychnine gave no test for phosphorus and that the others had about the same efficiency. A slight difference was observed, but before the question can be definitely settled the

¹ The suspensions always gave negative constants (see discussion of nephelometric constants in this paper).

² Further work with this grade of sodium molybdate was impossible, since we were unable to obtain it owing to the war.

experiments will have to be repeated. As our results below show, the reagent with 1 cc. of strychnine sulfate gave very satisfactory results, and until further data are at hand, it is best to adopt that amount.

Hydrochloric Acid.—To 15 cc. of water, 2.5 cc. of reagent (see directions, given below) and 5.00 cc. of KH_2PO_4 solution (5 mg. to a liter) were added varying amounts of normal hydrochloric acid and the volume made up to 40 cc. The table gives the nephelometric readings.

Amount of <i>N</i> acid, cc.....	17.5	10.0	5.00	2.50	1.25	0.00
Mm.....	19.4	15.5	14.4	13.9	14.0	14.0

Since the amount adopted for regular work is 1.25 cc. *N* under these conditions, almost four times as much may be used without decrease in the amount of precipitate. As may be seen, the results are also good when no acid is added in addition to that contained in the original reagent, thus showing a considerable latitude in the amount of free acid.

(b) **Directions.**—*Preparation of Sodium Molybdate.* Thirty-five and one-half grams of molybdic acid (c. p. free from ammonia, "100%") are boiled for about one hour with 50 cc. sodium hydroxide solution (containing 400 g. of 96% NaOH dissolved in 1 liter). The volume of liquid is brought up to 84 cc. with distilled water and the mixture shaken, until practically all of the solid sodium molybdate is dissolved. After adding a few grams of pure talcum powder and again shaking, the solution is filtered free from any residue, which in some preparations may be very dark. The filtrate, which should not have more than a slight yellowish tint, is evaporated¹ practically to dryness on the steam bath, and the residue washed, first, by grinding it with 40 cc. of 95% ethyl alcohol, filtering, and then by washing it on the filter with several portions of 20 cc. of alcohol. The residue, which should be perfectly white, is then dried in an oven at about 50° or in a vacuum desiccator.

Strychnine Solution.—Two grams of pure strychnine sulfate are put into a 100 cc. flask, with 80 cc. of water, and heated to about 90°. When the salt is completely dissolved, the solution is allowed to cool and then made up to the mark with distilled water.

Hydrochloric Acid (1-1).—Fifty cubic centimeters of strong HCl (sp. gr. 1.20) are diluted to 100 cc. with water; 5.00 cc. of this acid diluted to 100 cc. can be standardized by titrating with 0.5 *N* sodium carbonate. Twenty-four cc. of acid should be equivalent to 30 cc. of 0.5 *N* alkali.

Preparation of Reagent.—One and one-half grams of sodium molybdate (as prepared above) are dissolved in 2.5 cc. of distilled water and 10 cc. of (1-1) hydrochloric acid added while shaking. The precipitate which is formed on the first additions of acid redissolves in the excess of acid. One cubic centimeter of strychnine sulfate solution is then added while shaking, and the solution allowed to stand over night. After filtering, the solution should be perfectly clear and practically colorless. For this

¹ After concentrating for sometime the solution forms a crust of sodium molybdate, which must be broken up occasionally with a stirring rod.

purpose ordinary filter paper cannot be used, as the strongly acid solution extracts from it a substance which gives a very marked cloud on standing. This substance seems to be a phosphorus compound, as S & S No. 575, a hardened paper, and S & S No. 589 a quantitative paper, do not seem to give the slightest trace even on standing for weeks. S & S No. 597 gives a large amount of this suspension.

For Making Standard Solution.—One-tenth of a gram of KH_2PO_4 is dissolved in 2 liters of water; 100 cc. of this stock solution diluted to 1 liter will make a standard solution containing 5 mg. to a liter.

For Precipitating.—To 30 cc. of distilled water and 5 cc. of 0.5 N HCl, 5.00 cc. of reagent are added and the solution shaken thoroughly. Ten cc. of phosphate solution (standard or unknown) are then added slowly with a pipet; the mixture is shaken by gentle rotation of the flask, and after 3 minutes' standing it is ready for reading in the nephelometer.¹

For Reading the Instrument.—As these directions have already been given in detail, there is no need for repeating them here.¹

(c) **Results with New Reagent.**—As Pouget and Chouchak studied the effect of different salts on their nitric acid reagent, the experiments with the new reagent were limited to pure solutions of mono-potassium phosphate. In series of liquids, containing 5.0, 4.5, 4.0, 3.5, 3.0 and 2.5 mg. of phosphate, respectively, precipitates were produced as described in the directions and the readings plotted, as shown below.

Curve A (Fig. 1) was made September 11, 1914, with a reagent containing Merck's sodium molybdate and Curve B (Fig. 2) was made May 20, 1915, with a reagent containing a preparation of our own sodium molybdate, as indicated on page 2375.

Solution of KH_2PO_4 10 cc. sample contained		Curve A.		Curve B.	
Mg. KH_2PO_4 .	Mg. P.	Readings. Mm.	k.	Readings. Mm.	k.
0.0500	0.01140	13.92	..	14.74	..
0.0450	0.01025	14.95	0.29	15.92	0.24
0.0400	0.00911	16.40	0.23	17.26	0.23
0.0350	0.00797	18.10	0.21	19.00	0.22
0.0300	0.00683	19.90	0.21	20.90	0.22
0.0250	0.00569	22.00	0.21	23.00	0.22
		Average, 0.23		0.23	

The figures represent the average of 2 to 3 readings upon two or three solutions of each concentration and the relatively large constant indicates that the reaction is practically complete. (See Discussion.)

III. Discussion.

In nephelometric work published from the Harriman Laboratory thus far, considerable stress has been laid on the position of the curves obtained

¹ Kober, *J. Biol. Chem.*, 13, 485 (1913).

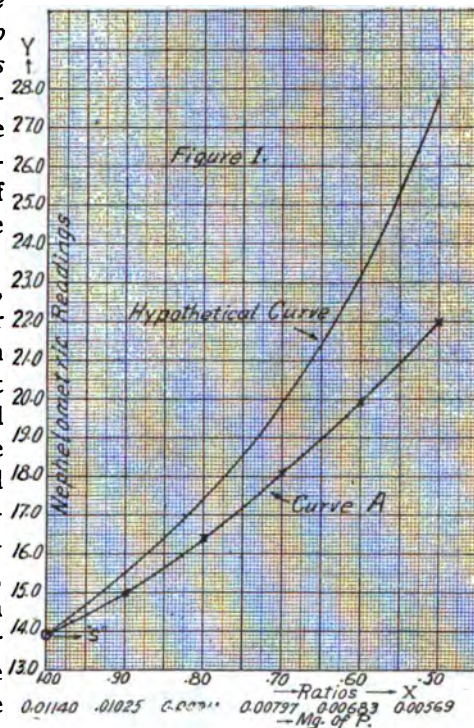
from a gradationed series of known solutions. These suspensions represent such small amounts of material that no other technic can be conveniently employed to determine the completeness of precipitation, and so we have relied only on the position of these curves, relative to the colorimetric curves, to tell us whether the precipitation is complete or not. As these curves are very important for rapid and accurate work, a recapitulation of their meaning and use will not be out of place here.

Taking Fig. 1 as an example, when the standard solution, after precipitation, was put on both sides of the instrument, the right side was set at 15.0 mm. and when the light in the eye-piece is matched, the left side reading is 13.92 (this reading, 13.92, is denoted by "s" in the nephelometric formula and curve). Now, having the standard solution¹ on the right set at 15.0 mm., another solution (0.900 as strong as the standard) was put in place of the standard on the left side, which

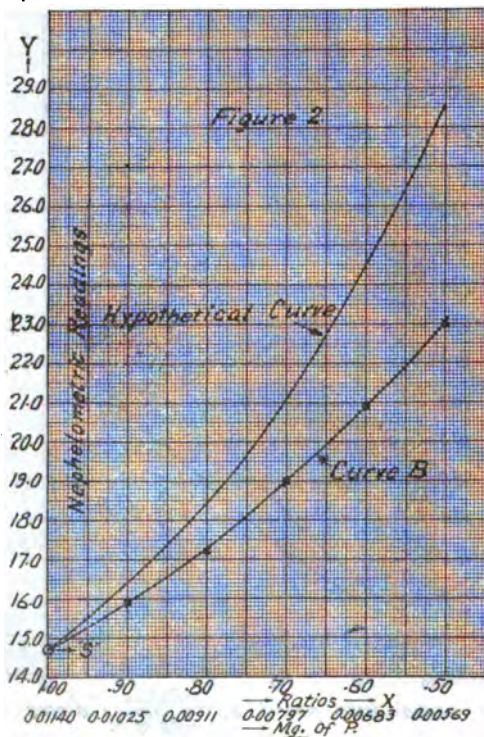
being matched with the standard remaining on the right side, gave a reading of 14.95 (this and similar readings are denoted by "y" in the formula and curve). Then solutions of 0.800, 0.700, 0.600, and 0.500 standard strength were put on the left side and matched successively, thus giving, respectively, 16.40, 18.10, 19.90, and 22.00 mm. A line drawn through these points gave us Curve A, and similarly Curve B was obtained.

If the instrument and light remained constant so that the readings of the standard solution always remained the same, in this case, 13.92 mm., the curve would be sufficient for practical work. The readings of known solutions, by reference to the curve, could be expressed directly in milligrams of substance. But most instruments do not remain constant (not even a good balance) and therefore the readings of standard

¹ By using "s" as the potential height of the standard liquid, any inequality in light, tubes, and plungers of the two sides is eliminated. It is similar to weighing by substitution.



on the left side (the readings of the right side being the same, usually 15.0 mm.) changes, from time to time, similarly to the zero point of the balance, and the value of the curve itself is thereby destroyed. Therefore,



we always check up the "zero-point" of the instrument, before beginning a series of analyses, by putting standard solution on both sides of the instrument and making readings.

To circumvent this difficulty of changing instrument, without using a nephelometric formula, two methods are available: (1) to redilute either the standard or the unknown solutions until they give the same readings. Unless the two readings are identical, which is difficult to obtain, an assumption or hypothesis must be introduced to finish the calculation, *i. e.*, that the readings are inversely proportional to the concentration of the substance, as in the curve marked "hypothetical." However, this assumption

and how near the readings of the "unknown" must be to those of the standard solutions to avoid appreciable error, can be seen at a glance by the difference between the hypothetical and the actual curve (A). Therefore, this way is not only tedious, but not very accurate. (2) The second way to obviate the inconstancy of the instrument, is, of course, to make a fresh curve each time, which again is unnecessarily tedious.

If a nephelometric curve could be expressed by an equation, any change in any one of the variables (*i. e.*, the readings) would be of no consequence and in general, the behavior of the reagents could then be followed and expressed with ease. This has been attempted¹ in the formula

$$y = \frac{s}{x} - \frac{(1-x)K}{x^2}$$
, where y = height of "unknown" solution, on the left side of the instrument, when standard solution is kept on the right side at a definite height, s = height of standard solution on the left side and x = the ratio of the concentrations of the two solutions. K = a

¹ Kober, *J. Biol. Chem.*, 13, 485 (1913).

constant, obtained by substitution of standardization values of s , y , and x .

When K obtained with one height of standard solution is compared with that of another height, it is found that K is proportional to the height of the standard solution, and the equation then becomes for any heights of liquid within moderate limits

$$y = \frac{s}{x} - \frac{(1-x)sk}{x^2} \text{ where } k = \frac{K}{s}.$$

When solved for x the equation becomes

$$x = \frac{s + sk + \sqrt{(s + sk)^2 - 4sky}}{2y}.$$

This equation, then, actually expresses the mathematical relationships between the ratios of the concentrations of the substances and the readings, and k , which is constant for a given substance and its reagent or precipitant, is an index of the amount of deviation of the readings from the colorimetric or hypothetical curve. Its value in the colorimetric curve is zero and the maximum thus far obtained for suspensions is 0.29.

One of us (K.) conjunctively with Sara S. Graves has found it convenient to estimate the maximum deviation or constant possible from a given suspension. This can be obtained by precipitating a standard solution, then diluting an aliquot portion with more reagent to a definite volume, and comparing the two suspensions in the nephelometer. The readings of " y " in this case will be slightly lower, and the constant slightly greater than the one used in actual analysis, or that obtained by diluting the solution before adding the reagent. This is due to the fact that when substances are precipitated in very dilute solutions, a small and often an appreciable amount remains unprecipitated, through its solubility or hydrolysis, but by precipitating before diluting, this solubility of the substance is eliminated, *as both standard and "unknown" or weaker solution then contain, as under ideal conditions, the same proportion of precipitated and dissolved substance.*¹ We shall hereafter designate it as the *theoretical constant of a substance*, and the difference between it and the actual constant may then be taken as representing the amount of substance not precipitated, under the conditions of analysis.

With the Graves reagent for ammonia it was found that the theoretical constant was 0.26² and the actual 0.14.³ For this new reagent for phos-

¹ It is, of course, probable that the suspension in the weaker solution will redissolve or hydrolyse slightly, until the same equilibrium is reached as in the one precipitated after dilution, but the speed of solution, near the saturation point, as is well known, is extremely slow, and any error due to this must be negligible.

² From the note book of S. S. Graves, dated February 10, 1915.

³ Even if the amount not precipitated is appreciable, no error in analysis results, as it is eliminated through standardization.

phorus, the theoretical constant was found to be 0.23, and the actual as shown above is near 0.22 (the average, including two high values was 0.23), which demonstrates that the precipitation of phosphorus in this extreme dilution is remarkably complete. (The half standard solution contained 1 part of phosphorus in 2,000,000, while the final suspension in the nephelometer only contained one part in 10,000,000.)

Another point to be considered in connection with the completeness of precipitation is that of stability of the suspension. Experience has shown that the more complete a precipitation the less stable the suspension, *i. e.*, the quicker it agglutinates. Thus it is sometimes necessary to sacrifice somewhat on the completeness of the precipitation to gain stability of suspension (*i. e.*, time for making readings). These and other properties of opalescent solutions will be taken up in detail in the near future.

IV. Applications.

Our first intention was to apply the reagent to the estimation of phosphorus in various organic and inorganic substances, but lack of opportunity compels us to content ourselves with a few preliminary trials. As Pouget and Chouchak have already suggested and tried the nitric acid reagent for metals, ores and biological material, and Greenwald has shown that the same is useful for blood work, it will not be necessary to give many details and data for the purpose of showing its usefulness. The accuracy obtainable with the new reagent is shown by the nephelometric curves.

As the dilution of the solution for most phosphorus estimations is large, very few substances are likely to interfere with the reaction. In an extreme case re-solution of a phosphomolybdate might be necessary. As a rule, any solution containing phosphates, but no organic matter, may be used at once, provided the solution is neutral or slightly acid and free from turbidity.

Ten cc. of urine were digested, as in a Kjeldahl nitrogen estimation with 20 cc. of concentrated sulfuric acid and 10 g. of potassium sulfate until the solution was clear. After the melt had cooled it was dissolved in water and made up to 500 cc. Twenty five cc. of the solution, neutralized roughly with ammonia and filtered, made up to 200 cc. gave a solution of suitable dilution for nephelometric work. As this gave a suspension slightly stronger than the standard used, it was put on the right side of the instrument and the standard on the left was used as an "unknown." The ratio of the diluted urine to the standard is therefore equal to the reciprocal of x , in this case.

Titration¹ with uranium acetate gave 0.053 and 0.054 g. of phosphorus.

¹ For making these estimations, I am indebted to Dr. Thomas LeClair of Frazer & Co., Laboratory, New York City.

in 100 cc. of urine. Further work is of course necessary to determine which of these values is the more accurate, and if the conditions for the application of the nephelometric method are satisfactory. It is possible that the ammonia used for neutralization has a slight inhibitory effect, and that sodium or lithium hydroxide will give better results.

TABLE II.

s.	y.	Ratio of solution to standard = 1/x.	Mg. P. in 1 cc. solution (1 cc. of standard 0.001034 mg. P).	G. of P in 100 cc. urine (total vol. dilution for 100 cc. = 40,000 cc.).
14.8	(a) {			
15.0				
		17.35	Av., 1.218	0.001259
14.9	(b) {			0.0504
14.9				
		17.30	Av., 1.215	0.001256
	(c) {			0.0502
		17.4		
		17.5		
14.90		17.45	Av., 1.226	0.001267
				0.0507
				0.0504

VI. Summary.

1. The reagent of Pouget and Chouchak has been modified, so as to be: (a) stable, (b) colorless, (c) quantitatively and (d) nephelometrically applicable.

2. It is shown that 0.005 mg. of phosphorus in 10 cc. of solution, or one part of phosphorus in 2 million parts of water, is easily determined quantitatively with the nephelometer.

NEW YORK, N. Y.

NOTE.

Alternating Current Thermoregulators.—Davis¹ has recently described an alternating current thermoregulator, designed for operation on the usual 110 v., 60 cycle lighting current. In my description of a large incubator² a very similar system was described, differing mainly from Davis' in that a 200 ohm, main line, telegraph relay was used to break the circuit, this relay operating in series with a 10 watt lamp and being controlled by a "fire-alarm" thermometer. This system operated very well for several months, the only trouble it gave being that incident to the sparking at the mercury-platinum contact of the thermometer; replacing the thermometer with a thermoregulator of larger bore improved

¹ THIS JOURNAL, 37, 1520 (1915).

² J. Ind. Eng. Chem., 6, 939 (1914).

this, but it seemed best to replace the 110 volt current in the control circuit, and in accordance with the suggestion at the end of my note (supra) a Westinghouse bell-ringing transformer was connected with its primary across the main supply, and the relay and thermoregulator operating on the outside 24 v. secondary terminals. This arrangement has given practically no trouble, and is at present used on the large incubator described; on three gas-heated water baths, using the Bear electromagnetic gas valve; and on a large electrically heated air-current drier, taking about 30 amperes in the heating circuit; in the latter case the 200 ohm relay operating on the 24 v. circuit controls a branch of the 110 v. circuit which operates a large motor-starting relay ("Contactor") the coil of which takes 0.4 ampere. Two different makes of these contactors are at present in satisfactory use in this Institute, one A. C., as the other D. C. They are rather clumsy for handling currents of less than 15 amperes, and there would appear to be some demand in laboratories for a well-constructed relay operating on 110 v. A. C. or D. C., to control circuits carrying from 2 to 15 amperes—such relays do not appear to be made at present; the ordinary main line relay will usually take care of 15 amperes, though the lead to the armature may warm up a little.

I believe that the lower voltage at the break is a decided advantage; the little bell-ringing transformers take very little current, and one can operate a large number of such temperature-control circuits.

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THE DETERMINATION OF VOLATILE ESTERS IN CITRUS OILS AND EXTRACTS.

BY ALAN R. ALBRIGHT AND CHARLES O. YOUNG.

Received August 14, 1915.

I. Theoretical.—The citrus oils have been shown, by a large number of investigators, to be very complex mixtures, as is true of practically all of the volatile oils. The principal representatives of the class, lemon and orange oils, are very similar in composition.¹ Each contains over 90% of hydrocarbons, the terpene *d*-limonene being in preponderance. Aldehydes constitute about 4–6% of lemon oil, about 1–3% of orange oil. Citral is the most important member of this group present, but is accompanied by smaller proportions of citronellal and other aliphatic members such as nonyl and decyl aldehydes. A number of other substances are present, to which some of the finer characteristics of the odor of the oils are due. The most important of these are the esters, the identity of which has been fixed as linalyl and geranyl acetates.²

¹ "The Volatile Oils," by Gildemeister & Hoffman.

² Umney and Swinton, *Pharm. J.*, 61, 196, 370 (1898).

Fairly satisfactory methods have been elaborated for the examination of the oils, in so far as regards the physical properties and the aldehyde content, but we have thought that a knowledge of the proportion of esters present would be an aid in forming judgment of these oils. In regard to lemon oil, some work has already been done in this field, and the following data are available:

Unmey and Swinton¹ report on an examination of lemon oil, giving an account of a process which involves the distillation of the terpenes *in vacuo*, removal of the aldehydes from the remaining oil by means of sodium acid sulfite, saponification, and fractional distillation to isolate the alcohols. The statement is made that pure oils contain from 1.2 to 1.4% of esters, calculated as geranyl acetate. We consider the process to be too involved to be a generally useful method of examination, and believe the quantitative separation of the aldehydes by the acid sulfite method to be practically impossible.

Berté states that the saponification number of the evaporation residue of a lemon oil should not exceed "3.5%," a higher figure indicating added fats.²

A. Parrozzani³ has recently published the results of some examinations of "terpeneless" lemon oils. The "terpene-free" oils are distilled with steam, and the aldehydes removed from the distilled oil with acid sulfite, but beyond these statements nothing is said regarding the procedure followed in the ester determination. Parrozzani gives the ester content of five of these concentrated oils, the range being from 26.1% to 37.2%, calculated as linalyl acetate. He believes that the ratio between the ester and the aldehyde content should be useful in judging a terpeneless oil.

II. Material.—The material upon which our experimental work was done consisted, first, of mixtures of known composition, which were made up as follows:

(1)	linalyl acetate	2.5%	citral	4%	limonene	93.5%
(2)	"	"	2.0	"	4	" 94.0
(3)	"	"	1.5	"	4	" 94.5
(4)	"	"	1.0	"	4	" 95.0
(5)	"	"	0.5	"	4	" 95.5

The linalyl acetate, obtained from Fritzsche Bros., had been stored under conditions favorable to its preservation. It showed an ester content of 85.3%. The citral was a fresh sample, purchased from Fritzsche

¹ *Loc. cit.*

² *Boll. chim. farm.*, 43, 709; through *Chem. Zentr.*, 1904, II, 1670. The exact meaning of the term "3.5%" is not stated in the abstract. The original has not as yet become available.

³ *Ann. R. Stas. Sperim. Acireale.*, 2, 86 (1914); abstract *J. soc. chem. ind.*, 34, 301.

Bros. The limonene was obtained from lemon oils by fractional distillation *in vacuo*, as described below, and it had an apparent ester content, after neutralization, of 0.46%, calculated as linalyl acetate. Considering the fact that practically no limonene remains in the sample after the fractional distillation, the effect of this amount of saponifiable matter on the determination of esters in the mixtures made up with these terpenes is negligible.

Further, experimental work was done upon samples of Sicilian lemon oils taken from regular importations; and upon some samples of terpeneless lemon extracts, partly commercially made, partly prepared in the laboratory.

III. Method.—For the determination of volatile esters, the authors propose the following manipulation:

First, the terpene fraction is removed as follows: 100 g. of the oil are weighed into a 3-bulb Ladenburg flask, the flask hung in a hemispherical iron air bath, connected with a pump producing a vacuum of 2–5 mm., a small flame placed below, regulated to give a slow rate of distillation, (not exceeding 18–20 drops per minute), and the process not disturbed until limonene ceases to come over.

When the automatic stopping of the vacuum distillation has taken place, the flask is connected with a long condenser, and a current of steam passed through until the volume of the distillate reaches 200 cc. This distillation is so regulated as to consume at least 30–45 minutes. The volume of material in the flask is kept as nearly constant as possible by heating with a flame. When the steam distillation is carried out in less time than this, it is almost invariably found that a sufficient amount of less readily volatile material is driven over to produce murkiness and to interfere seriously with the titration. The same effect is observed when the volume of oil with water in the flask becomes too low. When a large volume of water accumulates in the flask, the results appear to be too low, due to incomplete volatilization of the ester. The steam distillates are always found to be slightly acid to phenolphthalein, but no relation between this acidity and the saponification value has been observed.

A concentrated aqueous solution of the theoretical quantity, or an excess of semicarbazide hydrochloride with an equivalent amount of crystalline sodium acetate is now added. This is calculated from the aldehyde content, determined previously by Hiltner's method.¹ When an insufficient amount is used, the end point is not sharp. 100 cc. of 95% alcohol are then added, the mixture shaken around for a few minutes, and allowed to stand for 10–15 minutes, or longer, if convenient. A large bulk of citral semicarbazone usually separates at this point. The solution is then neutralized to phenolphthalein, 50 cc. 0.5 *N* alcoholic KOH added,

¹ U. S. Dept. of Agr., Bur. of Chem., *Bull.* 132, p. 102; *J. Ind. Eng. Chem.*, 1, 798.

and the solution boiled under a reflux for two hours. At the end of this time it is cooled to room temperature without delay, under tap water, and the excess alkali titrated with 0.5 *N* hydrochloric acid. It is necessary to use a much larger quantity of phenolphthalein than in ordinary titrations. Using a 100 g. sample, the number of cc. of 0.5 *N* alkali consumed, multiplied by 0.098 (the value in grams of 1 cc. 0.5 *N* linalyl-acetate), and an empirical factor (see below) gives the percentage of saponifiable matter present, calculated as linalyl acetate.

The above described process, when applied to lemon extracts, takes the following form:

400 g. are distilled slowly from an ordinary side-neck flask until the volume is reduced to 50–75 cc. Steam is then passed through until no more volatile oil comes over. The combined distillates are then treated exactly as the steam distillate in the case of lemon oils, calculating the necessary amount of semicarbazide from the citral value (1 g. citral requires about 0.75 g. semicarbazide hydrochloride).

IV. Experimental.—In the course of our preliminary work certain points were established, to which attention is called. Since it was recognized that aldehydes, on heating with alkalis, tend to resinify, or polymerize, and consequently combine with some alkali, experiments were carried out with a view to their quantitative removal. Neither sodium acid sulfite nor neutral sulfite could be made to serve this end. Precipitation and removal of the aldehydes as semicarbazones was then tried but this failed, as it was found impossible to wash the precipitate completely free of absorbed ester. This was manifest on saponification of the washed precipitate. That the consumption of alkali was due to ester, and not to a splitting of the semicarbazones, was shown by heating with excess of 0.5 *N* KOH, a preparation of pure citral semicarbazone, made from the commercial article in the usual way. Titration of the uncombined alkali showed a negligibly small apparent ester content.

Our experiments prove, then, that if the aldehydes be first condensed with semicarbazide, they do not resinify, and the semicarbazones are not hydrolyzed during the saponification of the esters with alkali, so that *condensation with semicarbazide is recommended as a general procedure as a preliminary to determination of the saponification value, when aldehydes are present.* Much trouble had been encountered, at first, in judging the phenolphthalein end point in the titrations, owing to the extreme murkiness of the solutions, and it was expected that when the aldehydes had been disposed of, the saponification solutions would remain clear and practically colorless. It was soon found, however, that the aldehydes were not alone responsible for our failures; only after the volatile part of the concentrated oil remaining after the vacuum distillation had been distilled out with steam, and the free aldehyde group protected

by condensation, could a satisfactory saponification be effected. It is evident, then, that the nonvolatile, or resinous, parts of the oil must be separated before the determination of the volatile esters is attempted. These resins themselves have a saponification value, as shown by the following experiment: The total nonvolatile matter from 100 g. of one lemon oil weighed 2.6 g. This showed, on saponification, an apparent linalyl acetate content of 1.15 g., or 1.15% of the original oil; calculated to the residue, this was 44%. The end point was very difficult to determine. This material, since it is not volatile either *in vacuo* or with steam, cannot be regarded as either linalyl or geranyl acetates; its composition is for no means clear, and for these reasons we hold that the determination of the esters should be made only in the volatile parts of the oils.

The amount of linalyl acetate, calculated from values obtained upon saponification of the pure ester under the best conditions, was found to be on the average 85.3% of that actually present,¹ while in carrying through our process, the average was 78.4%, indicating a constant loss of about 7% of the ester used in making up the mixture. The range was 77.4-80.3%. The saponification of linalyl acetate was carried out by heating 1.000 g. of the ester two hours under a reflux with 50 cc. 0.5 *N* alcoholic KOH, cooling at once and titrating back with 0.5 *N* hydrochloric acid to phenolphthalein.

To convert the apparent ester value, then, into a figure which will indicate almost exactly the true content of saponifiable matter, calculated as linalyl acetate, we multiply the former by $100/78.4 = 1.28$.

In Table I are given data relating to a few typical examples taken from thirty-eight experiments on the mixtures of known composition; in Table II, results of the application of the method to the commercial lemon oil mentioned above. The figures are given merely to indicate how close two successive trials have been made to check; fresh, authentic samples must be collected before limits may be set for the volatile ester content or for its relation to the aldehyde content. In Table III are given some data obtained in work on a few "terpeneless" lemon extracts.

As soon as authentic samples become available, work will be done on orange and other oils as well as on lemon oil, in order to establish limiting analytical figures. Extracts, especially those of the "terpeneless" type, will be prepared from these oils and examined in the same way. The possibility of developing a gravimetric method for the determination of aldehydes, making use of the insoluble semicarbazones is suggested. The authors propose to attempt to distinguish between lemon oil aldehyde and lemongrass citral by investigating the properties of the respective semicarbazones.

¹ According to Barillet and Berthel , equilibrium is reached when 85.5% of linalyl acetate is saponified with excess KOH. *Bull. soc. chim. de France*, 1915, 20.

TABLE I.—MIXTURES OF KNOWN COMPOSITION.

No.	Ester content. %.	Wt. sample. G.	Vacuum distillation.			Ester found. %.	Ester found. % theo- retical.	Ester found X 1.28.
			Pres- sure. Mm.	Temp. of distn. of bulk. °	Time. Hrs.			
34	2.50	100	3	31.0°	4	1.97	78.8	2.52
38	2.00	100	3	36.0°	3 1/2	1.58	79.0	2.02
66	1.00	100	3	..	4 1/2	0.77	77.0	0.99
67	1.00	200	6	0.79	79.0	1.01

TABLE II.—NATURAL LEMON OILS.

No.	Aldehyde content. % citral.	Wt. sample. G.	Vac. distn. Hours.	Ester found. %.	Corrected ester con- tent. %.	Ratio esters to aldehydes.
54001	5.4	100	3 3/4	1.32	1.69	0.31
54001	5.4	100	4	1.36	1.74	0.32
53933	4.9	100	4 1/2	1.05	1.34	0.27
53933	4.9	100	2 3/4	1.08	1.38	0.28
53955	4.8	100	4 1/2	0.99	1.27	0.26
53955	4.8	100	3 1/2	0.97	1.24	0.26

TABLE III.—"TERPENELESS" LEMON EXTRACTS.

No.	Wt. sample. G.	Vol. distillate. Cc.	Ester found. %.	Corrected ester content. %.
75	400	700	0.11	0.14
79	400	600	0.07	0.09
80	400	600	0.08	0.10

Summary.

The following method, in brief, is suggested for the determination of the volatile saponifiable matter, calculated as linalyl acetate, contained in citrus oils. The terpene fraction is distilled *in vacuo* from a large, say, 100 g. sample, and the remaining volatile oil removed by steam distillation. The aldehydes in the steam distillate are condensed with semicarbazide hydrochloride and the esters determined in the presence of the semicarbazone by saponification with KOH. The process is applicable to the corresponding extracts by distilling off all the readily volatile matter and treating this exactly as the steam distillate obtained in the examination of the oils. The manipulation described in the text should be adhered to.

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A STUDY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF OILS DISTILLED FROM THE VARIOUS PARTS OF THE PLANT ACORUS CALAMUS, L.

By G. A. RUSSELL.¹

Received August 3, 1915.

Acorus calamus, L., (Family Araceae) is found in the moderate zones of all the countries in the northern hemisphere, being indigenous to the

¹ Published by permission of the Secretary of Agriculture.

eastern half of North America, and found as far north as Nova Scotia. It grows usually in low, wet and boggy places. In the drug market it is known under the name of "calamus," the marketable portion of the plant being the unpeeled rhizome.

The cultivation of calamus is reported to have been conducted in Poland in the thirteenth century, and in Germany in the sixteenth century.¹ Clusius is reported as having cultivated calamus in 1574 from a root received from Asia Minor. He distributed the plant to other botanists in Belgium, Germany and France, from which latter place it was introduced into England in 1596, and there grown by Gerard. During the later centuries its cultivation has not been carried on to any great extent, the supply coming from natural sources.

Distillation of the oil of calamus has been carried on practically from the time the plant was first cultivated, mention of the distilled oil being found in the price ordinance of Frankfurt in 1582 and in the Dispensatorium Noricum in 1589.² A chemical examination of the oil was first reported by Wendel in 1718. Since then other investigators have from time to time reported on the volatile oil. These investigators do not give the origin of the oils examined, but they probably came from plants collected in the wild state.

During the seasons of 1913 and 1914 a small quantity of calamus was grown on upland soil at Madison, Wis. The plants flourished, and at the close of the season of 1914 they were dug and the various parts distilled with steam. The aerial parts were distilled while yet green and fresh. The rhizomes and roots were first air dried, then separated and distilled. The fresh aerial parts yielded on distillation 0.123% oil, the dried rhizomes 0.638%, and the dried roots 2.50%. In addition to these, a small quantity of air-dried rhizomes from Bell, Md., was distilled, and also a small quantity of dry rhizomes obtained in the open market. The former yielded 0.95% oil, and the latter 1.493%. The yield of oil from rhizomes, as heretofore reported, is greater than in any of the above. No doubt freshly dried rhizomes from plants grown in their natural habitat yield more oil than those which have laid in stock for some time. Compared with what has heretofore been reported, the yield of oil from the rhizomes purchased in the open market is low, the age of the samples probably accounting for the low percentage. The yield of oil from rhizomes grown on upland at both Madison, Wis., and Bell, Md., is much lower than any hitherto reported. These low yields are probably due to the fact that the plant was taken from its natural habitat and grown in entirely new environments.

¹ Bentley and Trimen, "Medicinal Plants," 4, 279 (1880).

² Gildemeister and Hoffmann, "The Volatile Oils," 1900, p. 301. Translated by Edward Kremers.

Physical Appearance of the Oils.—The oil from the fresh tops of calamus was straw yellow in color, with a pleasing aromatic camphor-like odor, and an acrid, spicy, somewhat bitter taste. The oil from the rhizomes grown at Madison, Wis., was light reddish brown in color. The odor was aromatic, somewhat camphoraceous, resembling the odor of the freshly dug rhizomes, and the taste acrid and bitter. The oil from the roots was golden yellow in color with a pleasant aromatic camphor-like odor and a pungent, bitter, acrid taste. The oil obtained from the rhizomes grown at Bell was similar in all respects to that produced at Madison, Wis. The oil from the rhizomes, obtained in the open market was brownish yellow in color, with a pungent, somewhat aromatic and slightly camphoraceous odor, and a pungent, bitter taste.

Physical Constants of the Oils.—The usual physical constants, density, specific rotation, and index of refraction, were determined. The results are tabulated in Table I.

TABLE I.
Physical Constants of Oils from *Acorus Calamus*. Chemical Constants.

Part distilled.	Geographic source.	Density at 23°.	$[\alpha]_D$ at 23°.	n_D at 23°.	Acid number.	Ester number.	Saponification number.	Acetylation number.
Tops	Madison, Wis.	0.9509	+12.2	1.5035	None	12.6	53.05
Rhizomes	Madison, Wis.	0.9547	+21.7	1.4990	None	15.5	38.40
Roots	Madison, Wis.	0.9491	+18.7	1.5065	None	23.7	42.10
Rhizomes	Bell, Md.	0.9938	1.5140	8.15 ¹	55.3	63.45
Rhizomes	Open market	0.9945	1.5080	5.75 ¹	42.5	48.25

From the density figures little comparison can be drawn as to the constituents of the oils; the range being between 0.9 and 1.0 indicates a mixture of terpenes and possibly some oxygen derivatives. The high specific gravity of the oils from the rhizomes grown at Bell and those obtained in the open market is partially due to age, the constant having been determined eight weeks after distilling.

All parts of the plant yield oils with dextrorotatory properties. Being optically active, all these oils must contain some compound, or compounds, with asymmetric carbon atoms. Owing to the small amounts of oil obtained from the other rhizomes distilled, an observation could not be made of their rotation.

The index of refraction of the oils from all parts of the plant lies within a very small range. All the oils have a low index of refraction, indicating the absence of compounds containing double bonds.

Solubility of the Oils.—Oil from the fresh aerial part of calamus was found to be soluble in 90% alcohol with turbidity in 5 volumes or over; soluble in 18 volumes of 70% alcohol and clear in excess.

Oil from the rhizomes grown at Madison was soluble in all proportions of both 90 and 70% alcohol.

¹ Determined eight weeks after distilling.

Oil from the roots grown at Madison was soluble in 6 volumes of 90% alcohol, and clear in excess, also soluble in 40 volumes of 70% alcohol and clear in excess.

Since terpenes and sesquiterpenes decrease the solubility, and oxygenated compounds increase the solubility of an oil in alcohol, a comparison of the oils from the various parts of the plant is made possible. The oil from the rhizomes was very soluble in 90% alcohol, that from the tops less soluble, and that from the roots still less soluble. This characteristic of the oils indicates that a greater portion of terpenes or sesquiterpenes is present in the oil from the roots than in either the oil from the tops or rhizomes, while of the latter two the oil from the tops contains the greater amount of terpenes or sesquiterpenes. The same characteristics are manifested when the various oils are dissolved in 70% alcohol. The higher solubility of the oil from the rhizomes, and the lower solubility of the oil from the tops and roots, is also probably due in part to the larger amount of oxygenated compounds present in the oil from the rhizomes than in either of the other oils used in comparison.

Chemical Constants of the Oils.—In determining the chemical constants the usual methods were employed and the usual determinations made. The results are tabulated in Table I.

No free acids were found in the freshly distilled oils from the various parts of the plant. An index to the rapidity with which free acids are formed in the oil from the rhizome is found in the acid numbers of the oils from the rhizomes grown at Bell, Md., and those secured in the open market, respectively.

Esters are found in all parts of the plant, as indicated by the values found. The greatest amount is found in the roots, the least in the tops. This would indicate that esters are formed more rapidly in that part of the plant furthest removed from air and light. That the ester value increases with storage is shown by the numbers obtained in the oils from the rhizomes grown at Bell and from those obtained in the open market.

In determining the acetyl value, the method as outlined in Gildemeier and Hoffmann¹ was followed. Alcohols are present in all the parts of the plant, being in greatest abundance in the tops and least in the rhizomes. This is made known by the saponification number found after acetylation, which in these oils is greatest in the oil from the tops. The values found point to the probability of the production of alcohols in those parts of the plant where the greatest activity is taking place, namely, the tops and roots.

Tests for Phenols and Aldehydes in the Oils.—A qualitative test for phenols gave negative results in all the oils, as did a quantitative test. The latter was made by shaking 5 cc. of oil with a 5% solution of sodium

¹ *Loc. cit.*

hydroxide and allowing the mixture to stand for 25 hours. No diminution could be noted in the volume of oil. The alkaline solution was then run off, acidified with sulfuric acid, and distilled with steam. The distillate tested with ferric chloride gave negative results in all the oils from the various parts of the plant. It is concluded, therefore, that no phenols are present in these oils.

A qualitative test for aldehydes by means of Schiff's reagent gave positive results in all the oils. In all cases 2 cc. of the reagent were used and one drop of oil. From the density of the color produced, an approximate comparison can be made of the amounts of aldehyde present. Oil from the tops gave the deepest coloration, followed by that from the rhizomes and roots, in the order stated. From this qualitative test it may be inferred that the production of aldehydes is greatest in the part of the plant exposed to the action of sun and air and that this production diminishes as these factors are more or less shut off.

Combined Acids in the Oils.—Owing to the small amounts of oils available for investigation, this determination was made on the oil just previous to fractionation. The oils were saponified with alcoholic potassium hydroxide, water added and the whole heated on a water bath until the alcohol was expelled. The oil which separates out was removed, and the aqueous alkaline solution shaken out with ether to remove any adhering oil. The alkaline solution was then evaporated on a water bath to a small volume, treated with an excess of sulfuric acid and distilled with steam. The distillate was tested for acidity with litmus paper and, where any oily globules separated, these were removed by shaking out with ether, the ether evaporated and the insoluble acids thus obtained neutralized with 0.02 *N* potassium hydroxide and precipitated with 0.1 *N* silver nitrate.

All the oils contain small amounts of soluble and insoluble acids in combination. The odor of the distillates was quite pronounced, but not extremely disagreeable, indicating that the acids were of comparatively low carbon content. An attempt to produce stable silver salts of the acids from the oils of the rhizomes and roots failed, although every precaution was taken to prevent immediate reduction. The oil from the tops was found to contain a soluble acid, butyric acid, and an insoluble acid, heptolic (Oenanthylic) acid.

Silver butyrate requires 55.3% Ag. Found 56.73%.

Silver heptolate requires 45.5% Ag. Found 44.89%.

Fractionation of the Oils.—The saponified oils were fractionated under 14 mm. pressure. Fractionation was carried on in a three-bulb Ladenburg flask and the heat was so regulated that the oils all distilled with approximately the same rapidity. Seven fractions were obtained from each oil. The small amounts of oil available and the small fractions obtained, made

it impossible to refractionate the fractions and precluded the chemical examination of the fractions obtained. The fractions as obtained and their physical constants are tabulated in Tables II, III, and IV, and indicated graphically in Fig. 1.

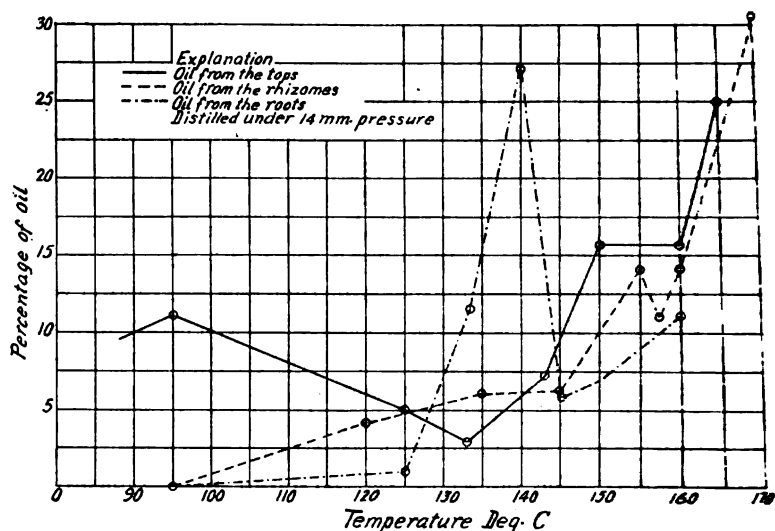


Fig. 1.—Fractionation curves of oils from the tops, rhizomes and roots of *Acorus Calamus*.

TABLE II.

Fractionation of the Saponified Oil from the Tops of *Acorus Calamus*.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D^{23}$ at 23°.	n_D^{23} at 23°.
1	1 to 95°	11.60	Water white	Limonene-like	0.8544	...	1.45
2	95-125°	5.12	Water white	Limonene-like	0.9198	...	1.45
3	125-133°	3.10	Water white	Camphoraceous			
4	133-143°	7.07	Water white	Camphoraceous, slightly disagreeable	0.9452	...	1.50
5	143-150°	16.72	Very pale straw, yellow	Decomp. odor	0.9695	+6.1	1.51
6	150-160°	16.17	Pale yellow	Decomp. odor, more pronounced	1.00880	+7.3	1.52
7	160-165°	24.93	Yellow	Decomp. odor, very pronounced	1.0317	+7.7	1.53
8	Over 165°	15.26	Deep reddish brown	Disagreeable

At 165° decomposition took place in the distilling flask marked by a sudden increase in temperature. The constituents of this oil are extremely high boiling, about 25%, boiling above 160° at the pressure of 14 mm. The indications point to a large amount of sesquiterpenes present in this oil.

¹ The oil begins to distil at 60°.

TABLE III.

Fractionation of the Saponified Oil from the Rhizomes of *Acorus Calamus*.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	N_D at 23°.
1	1 to 120°	4.17	Very pale straw yellow	Limone-like	0.9272	1.4793
2	120-135°	6.00	Very pale straw yellow	Camphoraceous	0.9381	+16.3	1.4870
3	135-145°	6.13	Very pale straw yellow	Somewhat disagreeable, decomp. odor	0.9420	+10.4	1.4938
4	145-155°	14.30	Pale straw yellow	Rather disagreeable, decomposed odor	0.9480	+4.3	1.5032
5	155-157°	10.95	Straw yellow	Rather disagreeable, decomposed odor	0.9585	+2.0	1.5055
6	157-160°	14.03	Straw yellow	Rather disagreeable, decomposed odor	0.9670	inactive	1.5072
7	160-170°	30.42	Greenish yellow	Rather disagreeable, decomposed odor	0.9883	-3.2	1.5112
8	Over 170°	13.93	Deep reddish brown	Decomp. odor

At 170° sudden decrease in the temperature marked a decomposition change taking place in the distilling flask. The oil is composed chiefly of high boiling constituents, probably sesquiterpenes, or closely related products.

In fraction two the greatest portion of the oil came over between 130-135°.

In fraction three the greatest portion of the oil came over between 135-140°.

In fraction four the greatest portion of the oil came over between 145-150°.

TABLE IV.

Fractionation of the Saponified Oil from the Roots of *Acorus Calamus*.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	N_D at 23°.
1	1 to 125°	0.918	Water white	Camphoraceous	1.5000
2	125-135°	10.97	Light straw	Borneol-like	0.9336	+24.1	1.5000
3	133-137°	21.25	Light straw	Camphoraceous	0.9346	+17.6	1.5038
4	137-140°	27.09	Light straw	Camphoraceous	0.9381	+19.1	1.5045
5	140-145°	5.79	Light straw	Camphoraceous	0.9443	+19.9	1.5060
6	145-150°	6.82	Light lemon	Decomp. odor	0.9503	+19.4	1.5082
7	150-160°	11.40	Lemon yellow	Decomp. odor	0.9710	+11.1	1.5130
8	Above 160°	15.75	Deep reddish brown	Disagreeable decomposed odor

At 160° decomposition takes place in the distilling flask marked by a sudden decrease in temperature.

The major portion of this oil distills below 140° and its composition is probably more or less terpenic in character.

Summary.

Acorus calamus cultivated on upland soil yields less oil than that grown in its natural habitat. All parts of the plant contain oil, the roots having the largest percentage.

¹ The oil begins to distil at 95°.

The oils obtained by steam distillation from the various parts of the plant, namely, aerial, rhizome, and roots, possess varying physical and chemical constants. The results of fractionation of these oils indicate that the components of each are present in varying amounts, also that these components vary to some extent.

Further work on the composition of these oils will be undertaken when larger supplies of oil are obtainable.

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WASHINGTON, D. C.

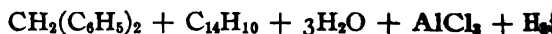
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

THE ACTION OF TRIOXYMETHYLENE ON *p*-XYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY RALPH C. HUSTON AND DWIGHT T. EWING.

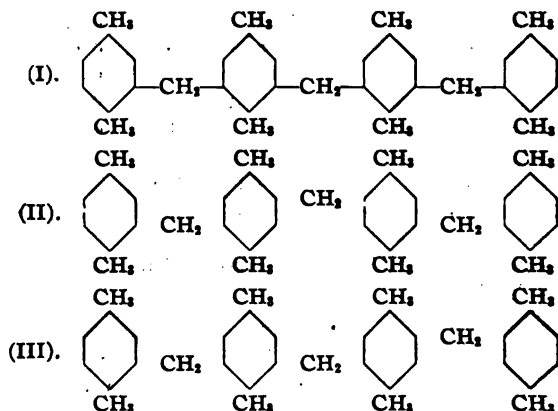
Received July 26, 1915.

Frankforter and Kokatnur,¹ as a result of their study of the action of trioxymethylene on benzene, toluene, *o*-xylene and mesitylene, in the presence of aluminum chloride, conclude that four benzene nuclei react with a molecule of trioxymethylene to form diphenylmethane, and anthracene or their homologues, hydrogen being liberated in the reaction.



In connection with other work on *p*-xylene which is being carried on in this laboratory an investigation of the behavior of this compound with trioxymethylene and aluminum chloride has been made.

The conditions of experiment were practically the same as those described by Frankforter and Kokatnur (see Experimental Part). From the resulting mixture, besides some unchanged xylene and a little toluene



¹ THIS JOURNAL, 36, 1529 (1914).

three compounds were isolated. The first of these was obtained in part by filtering the ether extract, and in part from the high boiling fraction of the same. It is a yellow crystalline powder melting at 204–205°, which was proven by analysis and *molecular weight determination* to have the formula $C_{28}H_{40}$. It is doubtless one of the preceding three possible tetra-nuclear compounds.

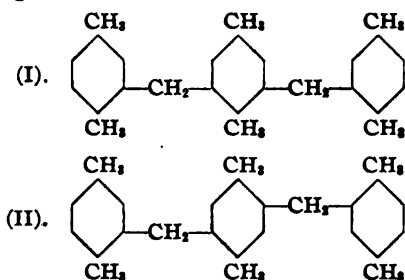
A glance at the following figures will show that simple analysis is not sufficient to fix the formula.

Calculated for tetramethyl anthracene, $C_{18}H_{18}$: C, 92.26%; H, 7.74%.

Calculated for the trinuclear compound, $C_{28}H_{40}$: C, 91.18%; H, 8.82%.

Calculated for the tetranuclear compound, $C_{38}H_{50}$: C, 91.24%; H, 8.76%.

The second compound formed the bulk of the fraction of the distillate from the ether extract which came over between 200° and 330°. It forms fine, colorless needles, which melt at 60° and is readily purified by recrystallization from alcohol. Analysis and molecular-weight determination correspond to the formula $C_{17}H_{20}$. The compound is then di-*p*-xylylmethane. The third compound distilled at a higher temperature than the dixylylmethane. Its melting point (157–158°) and solubility in organic solvents lies between those of the other two compounds. It forms clusters of very fine filaments which are absolutely colorless and which do not resemble the tetramethylanthracene described by Anschütz¹ in any way. The compound is probably a trinuclear compound having one of the following two formulae:



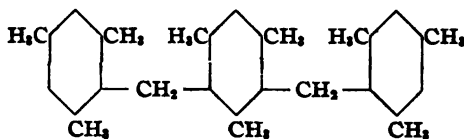
Unfortunately, it was not obtained in sufficient quantity for analysis. Aside from the fluorescence of the ether extract, there was absolutely no evidence of the presence of tetramethylanthracene.

It is of interest to note in this connection that some of the experimental data of Frankforter and Kokatnur may be interpreted in a different way than they interpreted them.

The formula assigned the compound, obtained from mesitylene, which melts at 286–287°, is especially doubtful.

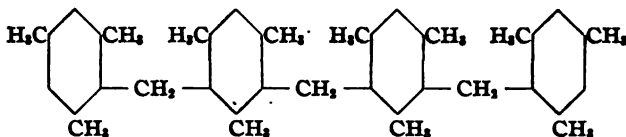
The analysis given (C 89.6%, H 8.45%) agrees more closely with the calculated percentages of the trinuclear compound

¹ *Ann.*, 235, 174 (1886).



Calc.: C, 90.57%; H, 9.43%.

or of the tetranuclear compound



Calc.: C, 90.63%; H, 9.37%.

than with those calculated for tetramethylantracene.

The description of the compound shows that it resembles closely the tetranuclear compound of *p*-xylene.

If the methyl groups of the mesitylene molecules are transformed by aluminum chloride in such a way that they form the central ring of the anthracene compound, it is difficult to conceive why Jones and Dewar¹ did not succeed in preparing it in that way.

The molecular weight of the compound was not determined.

Frankforter and Kokatnur² state that diphenylmethane and anthracene are formed in equal quantities and express in their equation the formation of a molecule of each of these from *one molecule* of trioxymethylene. In short, they assume that the molecule of trioxymethylene acts as such and not as formaldehyde, although they admit that similar condensations occur with hydrocarbons, CH_2O and H_2SO_4 . They conclude, since diphenylmethane does not yield anthracene when treated with trioxymethylene in the presence of aluminum chloride, that trioxymethylene does not act in the presence of aluminum chloride, like formaldehyde in the presence of sulfuric acid. This does not prove, however, that trioxymethylene does not act in the presence of aluminum chloride like formaldehyde in the presence of aluminum chloride. This last reaction has evidently never been studied. It further does not prove that the anthracene derivatives formed in certain cases, when benzene derivatives are treated with trioxymethylene in the presence of aluminum chloride, are not formed as the result of the decomposition of certain intermediate products such as phenylformol.³

Although we have not proven that the formation of anthracene is due to the decomposition of an intermediate product, we have proven conclusively that in the case of *p*-xylene, at least, diphenylmethane derivatives, and anthracene derivatives, are not formed in equal molecular amounts, as the equation of Frankforter and Kokatnur requires. We have further

¹ *J. Chem. Soc.*, 85, 219 (1904).

² *Loc. cit.*, p. 1533.

³ Nastukoff, *J. Russ. phys. chem. Ges.*, 35, 825 (1903).

shown the possibility of forming polynuclear compounds which contain as high as four benzene rings connected by methylene groups. This points to the dissociation of trioxymethylene into formaldehyde. It may be that steric hindrance prevents the formation of an anthracene compound from *p*-xylene, since the second connecting group must enter between two groups which are in the meta position to each other.

Experimental.

50 g. of *p*-xylene were added to 12 g. of trioxymethylene and the mixture was stirred by a motor for one hour. During this time 20 g. of anhydrous aluminum chloride were added in small portions. A large amount of hydrochloric acid was evolved. The temperature was carefully noted and was kept at approximately 45°, except for a moment, when it reached 60°. It quickly fell. If the stirring was stopped or if the aluminum chloride was added in rather large amounts a vigorous reaction would immediately commence. The color was first red but finally became reddish brown. The mass became so pasty that it was almost impossible to stir it. It was very fluorescent. After it had stood five days at about 0° the reaction appeared to be complete. Ice water was added to decompose the aluminum chloride and the mixture was treated with ether. The yellow precipitate was filtered off by suction and washed with ether.

Methylene bis-(di-*p*-xylylmethane), $C_6H_3(CH_3)_2CH_2C_6H_2(CH_3)_2CH_2C_6H_2(CH_3)_2CH_2C_6H_3(CH_3)_2$.—The residue was air-dried for six weeks, at the end of which time the odor of formaldehyde had disappeared. The resulting yellowish brown powder was recrystallized eight times from benzene. When the purified compound is heated to 196° it begins to darken. It melts at 204–205° with partial decomposition. It is readily soluble in benzene, chloroform and carbon tetrachloride, slightly soluble in ether, and insoluble in alcohol. With benzene it forms a reddish brown, slightly fluorescent solution. Yield, 1.8 g.

The molecular weight was found by the boiling-point method to be 463: theoretical, 460.

Calc. for $C_{28}H_{40}$: C, 91.24%; H, 8.76%. Found: C, 90.69%; H, 8.7%.

Di-*p*-xylylmethane, $C_6H_3(CH_3)_2CH_2C_6H_3(CH_3)_2$.—The fluorescent ether extract was distilled, two fractions being saved. The first, which was collected between 306° and 319°, was redistilled twice when most of it came over between 313–316°. On standing twenty-four hours it solidified. The solid is very soluble in benzene, ether and chloroform. It was recrystallized repeatedly from alcohol from which it crystallizes in long, white needles. M. p. 60–60.5°. Yield, 4.2 g. A molecular-weight determination by the boiling-point method gave 231; theoretical, 224.3.

Calc. for $C_{17}H_{20}$: C, 91.01%; H, 8.99%. Found: C, 90.92%; H, 8.95%.

The second fraction, which came over between 330° and 340° tended to solidify in the air condenser. A carbon-like residue remained in the distilling flask together with a light green fluorescent solid. This was extracted with chloroform and the extract added to the distillate. On evaporation of the solvent a precipitate formed which was readily soluble in benzene and chloroform, quite soluble in ether and rather insoluble in alcohol. It was recrystallized from a mixture of benzene and alcohol. It tends to form plate-like clusters of poorly formed filaments on the sides of the beaker. It is perfectly colorless and does not show the slightest fluorescence either in the crystalline form or in solution. M. p. $157-158^{\circ}$.

Anschütz¹ prepared 1,4,5,8-tetramethylanthracene from *p*-xylene and acetylene tetrachloride in the presence of aluminum chloride. It shows yellowish green fluorescence and melts at about 280° . It is evident that our compound is not identical with this tetramethylanthracene. Since but one tetramethylanthracene may be produced from *p*-xylene, it follows that our compound does not belong to that class. Since its properties are intermediate between those of di-*p*-xylylmethane and methylene-bis-(di-*p*-xylylmethane), it is thought to be a trinuclear compound, i. e., *p*-xylylmethyl di-*p*-xylylmethane. The yield was too small for a molecular-weight determination.

The mother liquor was evaporated to an oil which failed to yield more of the crystalline compound.

In a second experiment, 100 g. of *p*-xylene, 12.5 g. of trioxymethylene and 25 g. of aluminum chloride were mixed, and the above precautions were observed; the temperature rose to 62° . The upper portion of the mixture tended to take on a blue fluorescence. It was treated with cold water, and then with ether. A much larger yield of the tetranuclear compound was obtained here than in the other experiment (8 g.). This was filtered off and the ether extract was distilled. The first fraction came over between 60° and 150° and consisted of ether, benzene, toluene, and unchanged xylene. The second fraction was collected between 200° and 330° . On redistillation most of it passed over between 310° and 316° . The yield of di-*p*-xylylmethane was smaller than in the first experiment (2.4 g.). The next fraction was collected between 330° and 350° . It yielded an oily substance together with a small amount (0.2 g.) of the compound which melts at $157-158^{\circ}$. A fourth fraction was collected between 350° and 450° . This consisted of a small amount of a semi-solid mixture of an oil and solid. The oil was removed on a porous plate and the solid was recrystallized from benzene to which a little alcohol had been added. It was identified as methylene-bis-(di-*p*-xylylmethane). The residue in the flask consisted of a tarry mass with considerable carbon.

¹ *Ann.*, 235, 174.

Summary.

1. It has been shown that the reaction which takes place when *p*-xylene is treated with trioxymethylene in the presence of anhydrous aluminum chloride does not conform with the equation of Frankforter and Kokatnur.
2. Three new compounds resulting from the above reaction have been isolated and described. The molecular formulae of two of these have been determined and structural formulae are suggested.
3. It has been shown that molecular-weight determinations are essential factors in determining the formulae of substances of the types described.
4. The evidence at hand would seem to indicate that trioxymethylene is dissociated into formaldehyde, and this last is the active agent in the condensation reactions.

EAST LANSING, MICH.

THE ACTION OF TRIOXYMETHYLENE ON THE VARIOUS HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY G. B. FRANKFORTER AND V. KOKATNUR.¹

Received August 24, 1915.

Through the courtesy of the editor, we have just received a copy of a paper by Huston and Ewing, entitled "The Action of Trioxymethylene on *p*-Xylene in Presence of Aluminum Chloride," representing a line of investigation begun by us and on which we are working at the present time. As the paper referred to expresses doubt as to the conclusions drawn in our preliminary work,² we feel obliged to make a statement concerning our work, so that the readers of the JOURNAL, who are too busily engaged in their own chosen field to become thoroughly familiar with the details of our own, may grasp the general outline of our work and the relation of the paper by Huston and Ewing to it.

We indicated in our preliminary paper our intention to continue the work in this special field. We were therefore somewhat surprised to find that others should have taken up this work. We thought we made it clear that we intended to continue our work with other hydrocarbons, as we have done and are doing on both the aliphatic and the aromatic hydrocarbons. We were even more surprised at some of their conclusions. It appears that they question all our work on benzene, toluene, *o*-xylene, etc., from their work on *p*-xylene. If they do, it would be equivalent to questioning the formation of phthalic anhydride from *o*-xylene, because it is not so formed from *p*-xylene.

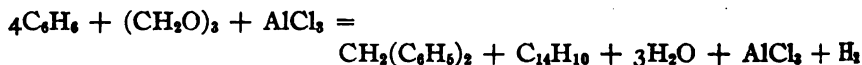
We wish to emphasize the fact that the object of our preliminary paper

¹ An explanation of our former paper of the above title.

² THIS JOURNAL, 36, 1529 (1914).

was: First, to determine whether or not the reactions studied by Kritchevsky and one of us¹ could be extended to other aldehydes, *e. g.*, trioxymethylene, etc.; second, to determine whether or not trioxymethylene derivatives analogous to those obtained by Grassie and Masseli,² could be prepared. We will state that we started out with formaldehyde, but soon changed to trioxymethylene because it seemed more interesting and especially because it was more convenient to work with, intending later on, if it seemed desirable, to take up formaldehyde. This has not yet been done in view of the fact that we were unable to obtain any of the oxy-compounds of trioxymethylene. It was assumed, therefore, that formaldehyde would probably form the same compounds as trioxymethylene. We have nowhere stated that trioxymethylene does not act in the presence of aluminum chloride like formaldehyde in the presence of aluminum chloride for the reason that we have not as yet studied formaldehyde.

That benzene and trioxymethylene in the presence of aluminum chloride form as a part of the reaction diphenylmethane and anthracene, there can be no doubt. Inasmuch as these two compounds were the principal ones which we isolated, we believe that we were justified in expressing their formation by the following equation:



We will state that we used the formula $(CH_2O)_3$ for the simple reason that we used trioxymethylene and not formaldehyde. Whether or not trioxymethylene will act like formaldehyde has nothing to do with the case.

We are quite as positive that ditoluyll methane and dimethylantracene are formed from toluene and trioxymethylene in the presence of aluminum chloride.

We are equally confident that dixylylmethane and tetramethylantracene are formed from *o*-xylene and trioxymethylene in the presence of aluminum chloride. As already stated, we did not determine the molecular weights of the above compounds inasmuch as they were identified as diphenylmethane and anthracene derivatives. Since reading Huston and Ewing's paper, however, we have made a molecular-weight determination of the compound which we designated as tetramethylantracene from *o*-xylene, a compound made for the first time by us. We found the molecular weight to be 219. The molecular weight of tetramethylantracene is 234.

Finally, from the conclusions drawn above, we felt justified in assuming that mesitylene would form an anthracene derivative, although we were

¹ THIS JOURNAL, 36, 1311 (1914).

² *Gaz.*, 28, 477.

not able to positively identify it. This work is still under way. It was delayed several months on account of the fact that we were forced out of the old laboratory before the new one was completed.

MINNEAPOLIS, MINN.

THE ACTION OF TRIOXYMETHYLENE ON *p*-XYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE. II.

BY RALPH C. HUSTON AND DWIGHT T. EWING.

Received September 6, 1915.

The editors have kindly forwarded us a copy of the preceding article by Frankforter and Kokatnur. In order that the position taken in our first paper on this subject may be more clearly defined we think it best to call attention to the following points:

1. It was not our purpose in taking up the work previously described by us to usurp the field of other investigators. The work was taken up in connection with other work on *p*-xylene which is being carried on in this laboratory. The results appeared to us to be worthy of publication.

2. We do not question the formation of diphenylmethane and anthracene derivatives when certain hydrocarbons are treated with trioxymethylene and aluminum chloride, but we have reason to believe that *both* are not *always* formed in appreciable amounts.

3. We do not believe that the equation of Frankforter and Kokatnur can be justified until it is shown by experimental data that diphenylmethane and anthracene derivatives are formed in equal molecular amounts. The fact that these derivatives are the principle ones isolated does not necessarily justify the equation.

4. Recent experiments in which toluene, trioxymethylene and aluminum chloride were used have led us to suspect that the relative yields of ditoluylmethane and dimethylantracene depend to some extent upon the temperature of the reacting mixture.

5. It was not our intention to give the impression that we were drawing conclusions as to the structure of the compounds described by Frankforter and Kokatnur from our work on *p*-xylene. We simply wished to point out that some of the experimental data presented by them might be interpreted in a different way.

6. We did not state in our previous paper that an anthracene compound can not be formed from mesitylene. It was shown that more than one interpretation might be placed on the data given.

EAST LANSING, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE AMERICAN MEDICAL ASSOCIATION.]

A NEW COLOR REACTION FOR PAPAVERINE.

By L. E. WARREN.

Received August 7, 1915.

In a study of the purity of commercial specimens of several of the opium alkaloids or their salts, a color reaction for papaverine ferricyanide was observed which, it is believed, has not hitherto been described. By modifications the test may be made to apply to the alkaloid, papaverine, or its commonly occurring salts, such as the chloride or sulfate, so that it seems probable that the reaction may prove of value in the identification of papaverine.

Papaverine is one of the minor alkaloids of opium. It occurs in Smyrna opium to the extent of about 0.8%, and in opium from other sources in amounts ranging from 0.2 to 1%. Papaverine is a weak base and is much less toxic than either codeine, morphine or thebaine. Formerly it was not used in medicine, but, owing to the recent pharmacological and clinical researches of Pal,¹ Popper,² Macht³ and others, it has attracted some attention from clinicians.

Papaverine is distinguished from the other of the more important opium alkaloids by the very sparing solubility of its ferricyanide in water and by the deep rose color which is slowly developed if the alkaloid be dissolved in sulfuric acid which contains a little formaldehyde⁴ (Marquis' reagent). A number of color reactions for papaverine are described in the older literature, but it has been shown by Pictet and Kramers⁵ that most of these are not due to papaverine but to cryptopine which, until recently, was present as an impurity in most commercial papaverine. At present, however, commercial supplies of papaverine and its salts contain only traces of cryptopine.

Papaverine ferricyanide was first described by Plugge.⁶ It is a pale lemon yellow compound which may be obtained as an amorphous precipitate by the addition with agitation of freshly prepared potassium ferricyanide solution to a faintly acidified, moderately dilute solution of a papaverine salt. Occasionally the precipitate separates in resin-like masses. From concentrated solutions narcotine and thebaine, if present, are also precipitated as pale yellow precipitates, the narcotine salt becoming green on exposure to the air. In dilutions above 1-500, papaverine

¹ *Wiener med. Wochenschr.*, 63, 1049 (1913); *Med. Times*, 42, 218 (1914).

² *Wiener klin. Wochenschr.*, 27, 361 (1914).

³ *J. Am. Med. Assoc.*, 64, 1489 (1915).

⁴ This reagent may be prepared by mixing 10 drops of 37% formaldehyde solution with 10 cc. of sulfuric acid. It should not be used if more than a week or two old.

⁵ *Ber.*, 43, 1329 (1910).

⁶ *Arch. Pharm.*, 225, 344 and 809 (1887).

alone is precipitated. This method was used by Plugge for the separation of papaverine from narcotine, the two alkaloids having been previously separated from thebaine by precipitation by a concentrated solution of sodium acetate.

The writer has observed that if the precipitate of papaverine ferricyanide, obtained as above described, be collected on a filter, washed with a little water and a small particle of the mass dissolved with stirring in a few drops of sulfuric acid which contains a little formaldehyde solution, a light blue color is produced at once; after a few minutes the color changes to bluish violet (sometimes purplish violet); if the solution be not further disturbed it becomes green at the edges and eventually becomes emerald green; on further standing the color fades to a dirty, brownish yellow or the solution may become nearly colorless. The reaction requires about 30 to 40 minutes for completion. Good results are obtained if about 0.001 g. of the dried papaverine ferricyanide be dissolved in about 0.1 cc. of Marquis' reagent. The reaction does not occur if sulfuric acid which does not contain formaldehyde be used, although a purplish color may be produced. Hexamethylenamine may be used in place of formaldehyde solution, although the initial color is somewhat slow in appearing and may be greenish blue rather than blue. Other reducing agents, such as formic acid, phenylhydrazine hydrochloride, sodium sulfite or sodium thiosulfate, if used in place of formaldehyde, do not give the reaction.

The test was applied to the ferricyanides of several of the alkaloids which form sparingly soluble ferricyanides. The cephaeline and emetine salts gave no colors; the narcotine salt gave a fugitive violet; the strychnine salt gave the well-known "fading purple" reaction. In the last two experiments the presence of formaldehyde did not appear to have any influence in the reaction, as the colors were given by the alkaloidal salts and sulfuric acid without that reagent.

The test was then varied by mixing finely powdered papaverine alkaloid with finely powdered potassium ferricyanide and stirring the mixture with Marquis' reagent. With some variations the succession of colors above noted, blue (greenish blue; see below), violet, green and brownish yellow, was produced, and the deep rose color, characteristic of papaverine with Marquis' reagent, did not appear. In this case it was noted that the initial color was a faintly greenish blue rather than a pure blue and in some instances the emerald green stage was not very pronounced, the violet being succeeded by the brownish yellow color. Potassium ferrocyanide can not be substituted for the ferricyanide in the reaction.

The test (alkaloid + potassium ferricyanide + Marquis' reagent) was then applied to a considerable number of alkaloids or their salts. In most cases either no color was produced or the color was not different

from the control in which no potassium ferricyanide was used. The substances studied were:

Aconitine, apomorphine hydrochloride, atropine sulfate, berberine hydrochloride, beta-eucaine lactate, brucine, caffeine, cephaeline hydrochloride, cinchonidine, cinchonine, cocaine hydrochloride, codeine, colchicine, coniine hydrobromide, dionine, emetine hydrochloride, mixed alkaloids from gelsemium, heroine, homatropine hydrobromide, hydrastine, morphine, narceine, nicotine, novocaine, physostigmine sulfate, pilocarpin hydrochloride, pseudomorphine, pyridine, quinine, sanguinarine nitrate, solanine, sparteine sulfate, strychnine, thebaine, theobromine, and the mixed alkaloids from veratrum.

None of the alkaloids tried except berberine, brucine, colchicine, hydrastine and physostigmine gave reactions differing markedly from the controls. Berberine gave a chocolate brown color, the control being lemon yellow; brucine, an orange-red color with colorless control; colchicine a reddish brown color with yellow control; hydrastine a brownish red color with colorless control; and physostigmine a pale, brownish yellow color with colorless control. No attempt was made to determine whether the color reactions noted with the last named alkaloids had been previously described or whether they were characteristic. In no case was there a duplication or simulation of the reaction with papaverine noted earlier in this paper.

The experiment with papaverine was then varied by substituting various oxidizing agents, such as ammonium vanadate, manganese dioxide, potassium permanganate, selenious acid, etc., for the potassium ferricyanide, in each case a very small quantity of the finely powdered reagent being well mixed with the finely powdered alkaloid and the mixture thoroughly stirred into a few drops of Marquis' reagent. Color reactions were given with a considerable number of the reagents tried, the colors in general being about the same as with potassium ferricyanide, with some individual variations in shade. Reactions were given by ammonium vanadate, cerium oxide, ferric ammonium sulfate, ferric chloride (solid), lead peroxide, manganese dioxide, phosphomolybdic acid, potassium bromate, potassium chlorate, potassium dichromate, potassium iodate, potassium nitrate, selenious acid, silver nitrate, sodium ortho-arsenate and uranium nitrate. Of these, the colors produced by the iron, silver and uranium salts were not very satisfactory. Bromates, chlorates, and nitrates were, in general, found not to give good results, as the oxidation apparently was carried out too rapidly to give a satisfactory play of colors. Ammonium molybdate, ammonium persulfate, magnesium peroxide, phosphotungstic acid or mercuric oxide did not give the reaction. Of the oxidizing reagents tried ammonium vanadate, cerium oxide, potassium permanganate and selenious acid were, perhaps, as satisfactory as any.

One of the most striking reactions observed was obtained by using potassium permanganate as the oxidizer. A very small crystal of the

salt was crushed with a glass rod, about 0.0005 g. of papaverine intimately mixed with the powder and the mixture stirred into about 0.2 cc. of Marquis' reagent. A green color appeared which almost instantly became blue. This deepened into an intense violet-blue which after some time became bluish green, then green and later a dirty brown.

Each of the alkaloids to which the test had been applied, using potassium ferricyanide as the oxidizing agent, was then tested by separately employing ammonium vanadate and potassium permanganate. In no case was there a duplication of the papaverine reaction, although codeine and dionine gave colors which were somewhat confusing. By making comparisons with papaverine, however, distinct differences were observable.

After the work recorded above had been completed the author received from Professor John Uri Lloyd a specimen of an unnamed alkaloid (possibly a mixture of alkaloids) which Professor Lloyd had separated from sanguinaria. The author also prepared the alkaloidal material according to the directions of Professor Lloyd from sanguinaria extracts sent by him for the purpose. On applying the papaverine test to this alkaloidal separate it was found that with certain oxidizing agents the succession of colors produced was somewhat like that with papaverine. Consequently some confusion might result unless comparison tests be carried out with known papaverine. With sodium ortho-arsenate, manganese dioxide, potassium dichromate and potassium iodate the unnamed alkaloidal substance gave an intense emerald green color which soon showed bluish streaks and faded through green to a dirty, yellowish brown. With the same reagents papaverine gave a momentary greenish blue which passed through deep blue, violet-blue, to green and brownish yellow. However, if selenious acid be used as the oxidizing reagent the initial color produced by the unnamed alkaloidal separate is an intense purplish violet, instead of a fugitive greenish blue which becomes deep blue, as with papaverine. The unnamed alkaloid is further differentiated from papaverine by its solubility in ammonia water, the comparatively ready solubility of its ferricyanide in water, and by the purplish violet, instead of a deep rose color, which it gives with Marquis' reagent.¹

Although the number of alkaloids to which the newly described test was applied is too small to warrant the conclusion that the reaction described is characteristic for papaverine, yet the considerable number tested without duplication of the color succession leads the author to believe that the reaction may prove of value in the identification of papaverine.

¹ At the request of Professor Lloyd the properties of this unnamed alkaloidal separate from sanguinaria are being further investigated and the results will be reported in a separate paper.

Summary.

1. Very few characteristic color reactions for papaverine are known, the most satisfactory being the deep rose produced by Marquis' reagent.
2. By treating papaverine ferricyanide with Marquis' reagent a blue color is produced which passes through violet and green stages to a dirty, brownish yellow.
3. By treating a mixture of the alkaloid, papaverine, and potassium ferricyanide with Marquis' reagent an essentially identical reaction is produced, although the initial color is generally greenish blue.
4. Many other oxidizing agents may be used in place of potassium ferricyanide, the shades of color produced varying somewhat with the reagent employed.
5. The reaction is best observed by intimately mixing a very small quantity of papaverine with a very small quantity of an oxidizing agent, such as cerium oxide, phosphomolybdic acid or potassium permanganate, and stirring the mixture with a few drops of sulfuric acid containing a little formaldehyde.
6. Of thirty-nine alkaloids tested but one (unnamed alkaloidal separate from sanguinaria) gave colors which in any way simulated the reaction with papaverine.
7. By using selenious acid as the oxidizing agent the unnamed sanguinaria alkaloid (or alkaloids) may be differentiated readily from papaverine.

The thanks of the author are due to Professor John Uri Lloyd for specimens of alkaloids from gelsemium, tobacco, sanguinaria and veratrum kindly furnished by Professor Lloyd for the investigation. Also to Dr. Willis S. Hilpert for verifying some of the reactions.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXIV. THE INTERACTION OF HIPPURIC ACID WITH THIOCYANATES.

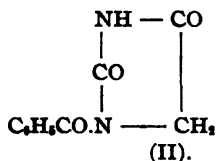
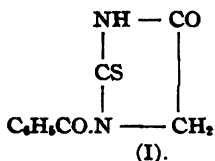
BY TREAT B. JOHNSON, ARTHUR J. HILL AND BERNARD H. BAILEY.

Received July 19, 1915.

Hippuric acid and dry ammonium thiocyanate interact very smoothly in the presence of acetic anhydride forming 2-thio-3-benzoylhydantoin¹ (I). Potassium thiocyanate likewise interacts to give the same hydantoin, but the yield is about 50% less than that obtained when ammonium thiocyanate is used.² Neither ammonium cyanate nor potassium cyanate interact with hippuric acid under similar conditions to give the corresponding 3-benzoylhydantoin (II).

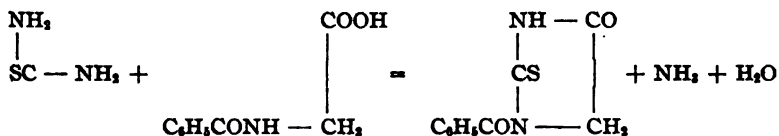
¹ Johnson and Nicolet, *THIS JOURNAL*, 33, 1973 (1911).

² Johnson, *Am. Chem. J.*, 49, 68 (1913); Johnson and Nicolet, *Ibid.*, 49, 197 (1913).



Brunner¹ has recently investigated the behavior of potassium cyanate and potassium thiocyanate towards acetic anhydride and finds that both salts interact with this reagent in a characteristic manner forming diacetamide $(\text{CH}_3\text{CO})_2\text{NH}$. The best yield of this compound was obtained by employing potassium cyanate and applying the reaction at ordinary temperature in ether. Furthermore, Brunner showed that this same salt likewise interacted with propionic, butyric, isobutyric and benzoic anhydrides forming the corresponding diacylamides. In the case of the potassium thiocyanate no statement is made regarding any transformations of the sulfur atom in this salt during the treatment with the anhydride. The behavior of ammonium thiocyanate towards acetic anhydride under similar conditions was not investigated.

Since the publication of our results on the abnormal behavior of potassium thiocyanate towards hippuric acid, as compared to that of the ammonium salt,² we have received, by correspondence and otherwise, several suggestions of possible explanations for this unique difference in reactivity. In our previous paper we did not attempt to offer an explanation, and stated that efforts would be made to obtain new data which would enable us to draw a more definite conclusion as to the mechanism of the reaction. One of the explanations that has been proposed is that the ammonium thiocyanate undergoes a normal rearrangement, when heated with acetic anhydride, giving primarily thiourea, which then interacts with the hippuric acid forming the 2-thiohydantoin (I). Such a condensation might be expressed as follows: There are three fundamental reasons



why this interpretation is not tenable. Firstly, such an explanation would necessitate the conception of an entirely different reaction-mechanism to explain the formation of the thiohydantoin (I) from an inorganic thiocyanate. The interpretation of this interesting transformation, which we have already proposed,³ is of general application and is based on the conception that thiocyanic acid is formed by action of the acetic

¹ Ber., 47, 2677 (1914).

² Johnson and Nicolet, *Am. Chem. J.*, 49, 197 (1913).

³ Johnson and Scott, *THIS JOURNAL*, 35, 1136 (1913).

anhydride and acetic acid on the thiocyanate. Secondly, ammonium thiocyanate does not undergo a rearrangement to thiourea when warmed with acetic anhydride and, thirdly, if thiourea was actually formed under such conditions it would not condense with hippuric acid, but interact immediately with the acetic anhydride at 100° giving acetylthiourea, $\text{CH}_3\text{CONHC(S)NH}_2$.¹ Kohmann² has recently shown that thiourea interacts with acetic anhydride, in the presence of hippuric acid, forming the monoacyl derivative $\text{CH}_3\text{CONHC(S)NH}_2$. He obtained no evidence of the formation of 2-thio-3-benzoylhydantoin.

We have investigated very carefully the behavior of acetic anhydride towards ammonium thiocyanate. According to the directions given by Nencki and Leppert³ and Klason,⁴ acetylpersulfocyanic acid is formed. We now find that if these two reagents (NH_4SCN and $(\text{CH}_3\text{CO})_2\text{O}$) are allowed to interact for a shorter time and at a slightly higher temperature, an entirely different result is obtained and *isodithiocyanic* acid is formed. A description of this interesting reaction is given in the experimental part of this paper. In no case did we observe the formation of monoacetyl- or diacetylthiourea,⁵ $\text{CH}_3\text{CONHC(S)NHCOCH}_3$. The results are all in accord with the assumption that thiocyanic acid is first formed when acetic anhydride and acetic acid interact with ammonium thiocyanate.⁶

Another suggestion to explain the difference in behavior between ammonium and potassium thiocyanates is that ammonium thiocyanate first interacts with acetic anhydride to form acetylpersulfocyanic acid,⁷ which then combines with hippuric acid to form the hydantoin (I). We are now able to state that such a change is not involved. No acetylpersulfocyanic acid is formed under the conditions of our experiments. Furthermore, if it was actually formed it would not interact with hippuric acid to form the thiohydantoin (I). Acetylpersulfocyanic acid is a very stable substance in the presence of acetic anhydride and no thiohydantoin (I) was formed after heating this compound with hippuric acid in acetic anhydride solution for 21 hours. In fact, practically all of the acetylpersulfocyanic acid used was recovered unaltered after such a vigorous treatment.

We have stated above that Brunner⁸ observed potassium cyanate to interact with a series of anhydrides to form the corresponding diacid-amides. In the light of this interesting observation it seemed of special

¹ Nencki, *Ber.*, 6, 599, 905 (1872); Prätorius, *J. prakt. Chem.*, [2] 21, 147 (1880).

² *THIS JOURNAL*, 37, 2130 (1915).

³ *Ber.*, 6, 902 (1873).

⁴ *J. prakt. Chem.*, [2] 38, 368 (1888).

⁵ Kohmann, *Loc. cit.*

⁶ Johnson and Scott, *Loc. cit.*

⁷ Nencki and Leppert, *Loc. cit.*; Klason, *Loc. cit.*

⁸ *Loc. cit.*

interest to us to determine whether other anhydrides besides acetic anhydride might be employed to effect a thiohydantoin condensation with hippuric acid. We have now applied the reaction with propionic and benzoic anhydrides and obtained with both reagents the thiohydantoin (I). In fact, propionic anhydride is just as efficient in producing the condensation as the acetic anhydride. We did not observe the formation of any propionylthiourea $C_3H_7CONHCSNH_2$. On the other hand, when benzoic anhydride was used only a small yield of the thiohydantoin was obtained, but a second product was formed which proved to be very interesting.

We now find that while part of the ammonium salt reacts as expected to form the thiohydantoin (I) the remainder undergoes a normal molecular rearrangement into thiourea, which then interacts with the benzoic anhydride giving benzoylthiourea,¹ $C_6H_5CONH.CSNH_2$. In fact, fully 50% of the ammonium thiocyanate undergoes the latter transformation. This interesting change is not due to the catalytic influence of the hippuric acid. We find that ammonium thiocyanate and benzoic anhydride interact smoothly at 100°, giving the same benzoylthiourea as is obtained when hippuric acid is incorporated. Therefore, we are dealing here with a normal rearrangement of the ammonium thiocyanate into thiourea, which then undergoes acylation, forming benzoylthiourea. In other words, *the benzoic anhydride acts catalytically*.

So far as the writers are aware no one has hitherto shown that ammonium thiocyanate can be rearranged to thiourea below 100°. It is a well-known fact that ammonium cyanate will change to urea at the temperature of boiling water but Reynolds² has shown that ammonium thiocyanate remains unchanged when subjected to such a treatment. He was the first to show that a rearrangement is produced by heating the thiocyanate at 170°. In fact, Reynolds³ states that ammonium thiocyanate changes very slowly when heated at its melting point (148–149°) and gives only 15.2% of its weight in thiourea after heating for 40 minutes. He has shown experimentally that the maximum proportion formed at a single operation is only 24.76% of the theoretical and that this is reached after heating at 170° for about 45 minutes. At 182° both the thiourea and ammonium thiocyanate begin to undergo decomposition and guanidine thiocyanate is formed with evolution of ammonia and hydrogen sulfide.

Dunstan and Mussell⁴ have recently reported data which they believe indicates that ammonium thiocyanate may rearrange to thiourea at a temperature below the melting point of this salt (148–9°). These investi-

¹ Pike, *Ber.*, 6, 755, 1107 (1873).

² Reynolds, *Ann.*, 150, 224 (1869).

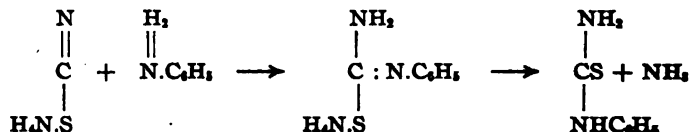
³ *J. Chem. Soc.*, 83, 1 (1903).

⁴ *Ibid.*, 99, 567 (1911).

gators observed that this salt and an excess of aniline interact at 130° forming phenylthiourea, $C_6H_5NHCSNH_2$, and state, in their paper, that the probable cause of the reaction is the primary formation of thiourea by rearrangement, which then reacts with the aniline giving the phenyl derivative. Such an interpretation, however, is not in accord with the known facts. Apparently Dunstan and Mussell¹ were unaware that Rathke had already investigated the behavior of both ammonium thiocyanate and thiourea towards aniline 26 years before the publication of their paper. Rathke wrote as follows:²

"Sodann habe ich jetzt beobachtet, dass eine concentrirte Lösung des gewöhnlichen Schwefelharnstoffs beliebig lange mit Anilin gekocht werden kann ohne dass eine Einwirkung stattfindet, während Rhodanammonium in gleicher Weise behandelt mit Leichtigkeit grosse Mengen des gewünschten Productes (Phenylthioharnstoff) liefert."

In fact, Rathke gave an interpretation of the mechanism of this transformation which is expressed by the following equation:



In other words, the formation of the phenyl derivative does not necessarily involve the primary rearrangement of the thiocyanate.

The latest contribution on this interesting problem is a recent paper by Sohn³ in which he describes the remarkable observation that aniline and ammonium thiocyanate do not interact in boiling, glacial acetic acid solution to form either *mono*-phenyl or *di*-phenylthioureas. On the other hand, diphenylurea is formed quantitatively with evolution of hydrogen sulfide. *The acetic acid therefore acts catalytically.* Urea and aniline likewise interacted in acetic acid solution forming the same substituted urea. Sohn also observed that the two reagents (thiourea and aniline) do not interact in the presence of acetic acid to produce phenylthiourea. Acetanilide only was formed under these conditions. In other words, this observation is in accord with that made by Rathke.⁴

In the case of this unique aniline-ammonium thiocyanate reaction, the evidence, so far obtained, therefore indicates that we are dealing here with a reaction-mechanism which does not involve a normal molecular rearrangement of the thiocyanate. We consider Rathke's and Sohn's observations of importance in their bearing on our speculations⁵ regarding the mechanism of our hydantoin reaction.

¹ *Loc. cit.*

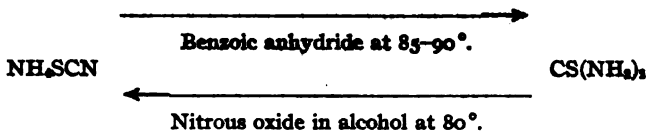
² *Ber.*, 18, 3105 (1885).

³ *Ibid.*, 47, 2438 (1914).

⁴ *Loc. cit.*

⁵ Johnson and Scott, *Ibid.*

The reverse change $\text{CS}(\text{NH}_2)_2 \longrightarrow \text{NH}_4\text{SCN}$ —is brought about by heating thiourea with water at 140° and also under the influence of catalytic agents. Claus¹ made the interesting observation several years ago that thiourea can be transformed into ammonium thiocyanate by saturation of an alcoholic solution of the urea with nitrous oxide. He found urea to be stable under similar conditions. Therefore, both ammonium thiocyanate and thiourea are susceptible to catalytic influence and their interconversion can be effected below 100° .



The study of these rearrangements will be continued.

We have now investigated further the behavior of inorganic thiocyanates towards hippuric acid in acetic anhydride solution. Ten different salts have been examined, namely, the four thiocyanates of the alkali metals NH_4 , Li, Na and K, the four thiocyanates of the alkali earths Mg, Ca, Sr and Ba and finally the two thiocyanates of Mn and Zn. Every one of these salts, with the exception of zinc thiocyanate, interacted normally with hippuric acid with formation of the thiohydantoin (I). The yields obtained, however, were not concordant. No salt examined reacted to give a yield of thiohydantoin (I) anywhere nearly equivalent to that obtained by application of the reaction with ammonium thiocyanate. The only combination besides the ammonium salt, that interacted to give a yield of thiohydantoin greater than 50% of the theoretical, was magnesium thiocyanate. The yield obtained in this case was 77% of theory while the yield of hydantoin was 93.4% when ammonium thiocyanate was used. The results of these experiments are recorded in the experimental part of this paper.

Experimental Part.

Acetypersulfocyanic Acid, $\text{C}(\text{S}.\text{COCH}_3)_2 = \text{N}-\text{S}-\text{C}(\text{S}.\text{COCH}_3)_2 = \text{N}.$ —

This cyclic compound was prepared by heating ammonium thiocyanate with acetic anhydride according to the directions given by Nencki and Leppert² and also by Klason.³

Reactions with Hippuric Acid in Presence of Acetic Anhydride.

Action of Acetypersulfocyanic Acid.—Two grams of hippuric acid (finely pulverized) and 2 g. of acetypersulfocyanic were suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid, and the mixture heated for 1 hour at 100° . There was no interaction of the

¹ *Ann.*, 179, 128 (1875).

² *Loc. cit.*

cyanic acid under these conditions. Nine cubic centimeters of acetic anhydride were then added and the heating continued for 20 hours at 100° . The liquid was then cooled and filtered when we recovered 1.7 g. of acetylpersulfocyanic acid, or 85.0% of the original amount taken. The acid filtrate was poured into 50 cc. of cold water and the solution evaporated to dryness. We obtained a semisolid substance which dissolved in warm sodium hydroxide solution. After filtering, in order to separate a little gummy material, the solution was acidified with hydrochloric acid. A crystalline substance deposited which melted at 121° . It was identified as benzoic acid. Acetylpersulfocyanic acid, therefore, does not interact with hippuric acid in acetic anhydride solution to form 2-thio-3-benzoylhydantoin.¹

Action of Potassium Cyanate on Aceturic and Hippuric Acids.—It has been shown that the *mono*-potassium salt of cyanic acid, $C_2H_3O_2N_2K$, is formed by the action of dilute acetic acid on potassium cyanate.² In order to determine whether a hydantoin would result by interaction of cyanic acid with hippuric acid in acetic anhydride solution, 2 g. of hippuric acid and 2 g. of potassium cyanate were suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid and this then heated on the steam bath. There was an immediate reaction on heating and a clear, yellow solution was obtained within a few minutes. On continued heating the mixture assumed an orange color and we obtained a thin magma of colorless crystalline material. After warming for 15 minutes the reaction product was poured into about 3 volumes of water, when a crystalline product separated. This crystallized from hot water in beautiful, rhombic prisms which did not melt at 300° . It did not contain potassium and was hydrolyzed by hydrochloric acid with formation of ammonium chloride. When digested with strong, hot alkali, ammonia was evolved. It sublimed when heated on a platinum foil. The compound was identified as cyanuric acid, $C_3H_3O_3N_3$. The filtrate above was evaporated and the residue recrystallized from water. Benzoic acid separated and melted at 121° . We obtained no evidence of the formation of 3-benzoylhydantoin. The similar behavior was observed when aceturic acid and glycoll were used instead of hippuric acid. Cyanuric acid was formed in both cases. We did not obtain 3-acetylhydantoin (m. p. 148°) which has previously been described by Harries and Weiss.³ It is of interest to note here that Brunner⁴ did not observe the formation of cyanuric acid when potassium cyanate was allowed to interact with acetic anhydride in ether solution.

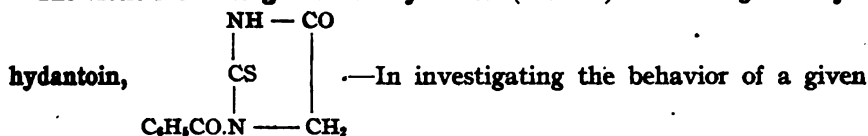
¹ Johnson and Nicolet, *THIS JOURNAL*, 33, 1973 (1911).

² Richter's "Organ. Chem.," I, 512.

³ *Ann.*, 327, 355 (1903).

⁴ *Loc. cit.*

The Action of Inorganic Thiocyanates (R.SCN). 2-Thio-3-benzoyl-



thiocyanate towards hippuric acid our procedure was consistent and was as follows: Two grams of the anhydrous rhodanide and 2 g. of hippuric acid were suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid. We then heated the mixture on the steam bath for one hour (in each case) and poured the resulting product into 50 cc. of cold water to decompose the acetic anhydride. Whenever the thiohydantoin was produced, it separated after pouring into water. This was dried and weighed. After separation of the thiohydantoin, the aqueous solution was then evaporated to dryness and benzoic acid separated from the residue by treatment with alkali. Whenever a small yield of thiohydantoin was obtained we found a corresponding large amount of benzoic acid in the filtrate. This resulted from hydrolysis of the unaltered hippuric acid with alkali. Ten inorganic salts were examined and the results, which we obtained, are recorded in the following table:

TABLE I.
Weight of
thiohydantoin (g.). Percentage of
theory.

Salt.	Weight of thiohydantoin (g.).	Percentage of theory.	Filtrate.
NH ₄ SCN.....	2.3	93.4
LiSCN.....	1.1	44.7	C ₆ H ₅ COOH
NaSCN.....	0.1	...	C ₆ H ₅ COOH
KSCN.....	1.1	46.7	C ₆ H ₅ COOH
Mg(SCN) ₂	1.9	77.2
Ca(SCN) ₂	0.6	0.24	C ₆ H ₅ COOH
Sr(SCN) ₂	1.2	47.8	C ₆ H ₅ COOH
Ba(SCN) ₂	0.6	0.24	C ₆ H ₅ COOH
Mn(SCN) ₂	1.0	40.6	C ₆ H ₅ COOH
Zn(SCN) ₂	C ₆ H ₅ COOH

Ammonium thiocyanate, as has been emphasized in a previous paper,¹ reacts to give the maximum yield of 2-thio-3-benzoylhydantoin. It is also an interesting fact that magnesium thiocyanate interacts the most smoothly of the thiocyanates of the alkali earth metals. No salt examined, with the exception of magnesium thiocyanate, reacted to give a yield of the thiohydantoin greater than 48% of the theoretical. No hydantoin was formed when zinc thiocyanate was used.

Action of Thiourea.—This experiment was conducted in the usual manner by warming 2 g. of thiourea and hippuric acid, respectively, with acetic anhydride and a small amount of acetic acid for 1 hour at 100°. After cooling and pouring into 50 cc. of cold water no thiohydantoin separated. The aqueous solution was evaporated to 100°, when we

¹ Johnson and Nicolet, *Loc. cit.*

obtained a semi-solid residue which dissolved easily in a small volume of 95% alcohol. On cooling, stout prisms separated which melted at 166-7°. This substance was identified as acetylthiourea. It dissolved in dilute sodium hydroxide solution and was precipitated unaltered by addition of hydrochloric acid. The substance gave a strong test for sulfur. The yield of purified material was 1.3 g.

Calc. for $C_2H_5ON_2S$: N, 23.7. Found: N, 23.4.

Action of a Mixture of Ammonium Thiocyanate and Thiourea.—

Two grams of a mixture, containing equal parts by weight of ammonium thiocyanate and thiourea, and 2 g. of hippuric acid were treated in the usual manner with 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid. After heating for 0.5 hour the resulting fluid was then poured into 50 cc. of cold water, when 0.9 g. of 2-thio-3-benzoylhydantoin separated. This is a yield of 81.0% of the theoretical. It crystallized from 95% alcohol in prisms and melted at 165°.

After filtering off the thiohydantoin, the acid filtrate was evaporated to dryness and the residue triturated with a small volume of cold water to dissolve ammonium thiocyanate. A product was obtained here which was insoluble in water. This crystallized from alcohol in prisms which melted at 167°. This material contained sulfur and was identified as acetylthiourea. A mixture of this substance with some acetylthiourea melted at the same temperature. The yield was 0.9 g. A theoretical yield would have been 1.5 grams.

Action of Ammonium Thiocyanate on Hippuric Acid in Propionic Anhydride Solution.

In this experiment the following proportions were used: 2 g. of the thiocyanate, 2 g. of hippuric acid and 10 cc. of pure distilled propionic anhydride. On heating the mixture at 100° the hippuric acid dissolved at once and the solution assumed a yellow color, which finally developed into a deep red. After one hour's treatment the solution was then poured into 50 cc. of water when the 2-thio-3-benzoylhydantoin separated. The yield of crude hydantoin was 2.4 g. It crystallized from alcohol in prisms which melted at 165°. In other words the thiohydantoin was formed just as smoothly in the presence of propionic anhydride as when acetic anhydride was used.

The Action of Potassium Thiocyanate.

An attempt to prepare the thiohydantoin by the action of potassium thiocyanate on hippuric acid in propionic anhydride solution was unsuccessful. On pouring the reaction mixture into water only a gum was obtained. This refused to crystallize, and on trituration with alkali gave a small amount (0.5 gram) of benzoic acid.

The Action of Benzoic Anhydride on Ammonium Thiocyanate.

Two grams of the thiocyanate and the same quantity of benzoic anhydride were heated together for an hour on the steam bath (temperature

of solution 85–90°). The anhydride, on melting, dissolved the thiocyanate forming a light yellow solution without evolution of hydrogen sulfide. On pouring the resulting mixture into 50 cc. of water a yellow, crystalline substance separated. This was separated by filtration and triturated with a small volume of dilute, aqueous ammonia when only part of the material dissolved. The insoluble material (0.6 g.) contained sulfur and crystallized from hot water in prisms which melted at 176°. This substance was identified as benzoylthiourea. A mixture of this product with some benzoylthiourea¹ melted at the same temperature.

The ammoniacal solution was acidified with hydrochloric acid when benzoic acid separated. This melted at 121°.

The Action of Benzoic Anhydride on Ammonium Thiocyanate in the Presence of Hippuric Acid.

The following proportions were used in this experiment: 10 g. of benzoic anhydride, 2 g. of hippuric acid and 2 g. of dry ammonium thiocyanate. The three substances were thoroughly mixed and then heated in a water bath at 100°. The mixture completely liquefied, giving a clear solution which became red on prolonged heating. A slight effervescence was also observed and benzoic acid sublimed from the solution. After heating for 1 hour the mixture was poured into 50 cc. of water when a semi-solid substance separated (filtrate was saved). This was dark red in color and dissolved in ether with the exception of a very small amount of material which was not examined further. After evaporation of the ether the residue was then triturated with dilute aqueous ammonia when only part of the material dissolved. This contained sulfur and crystallized from water in small prisms which melted at 176°. It was identified as benzoylthiourea. The yield was 1.0 g.

The ammoniacal solution was acidified with hydrochloric acid, when benzoic acid, melting at 121°, separated. The filtrate mentioned above was evaporated to dryness and the residue was crystallized from water. The only substances isolated in a state of purity were ammonium thiocyanate and benzoic acid. We obtained here 0.7 g. of this acid. We did not obtain evidence of the formation of any 2-thio-3-benzoyl hydantoin.²

The Formation of Isodithiocyanic Acid by the Action of Acetic Anhydride on Dry Ammonium Thiocyanate.

Isodithiocyanic Acid, NH.CS.NH.CS .—Ten grams of ammonium

thiocyanate (previously dried at 110°) were suspended in 14 g. of acetic anhydride in an 8 oz. flask. The latter was connected with a return condenser and the mixture protected from moisture while it was heated on the steam bath. There was an immediate reaction on heating with solution of the thiocyanate and constant evolution of gaseous products

¹ *Loc. cit.*

² Johnson and Nicolet, *Loc. cit.*

among which hydrogen sulfide was identified. A clear solution resulted. Within two or three minutes, however, this commenced to become quite turbid, and within 15 minutes a considerable quantity of orange-colored material had deposited. Heating was discontinued at the end of 3 hours and the reaction mixture allowed to stand at room temperature for 12 hours. The orange-colored product, weighing 1.8 g., was then filtered off and the anhydride solution concentrated to a small volume and poured into cold water. After standing a short time this aqueous solution deposited 0.5 g. of material which afterwards proved to be identical with the substance which separated from the original anhydride solution. This compound was quite soluble in sodium hydroxide solution, from which it was precipitated unchanged by dilute hydrochloric acid. It was very difficultly soluble in cold water, but somewhat soluble in hot, and separated on cooling in characteristic yellow balls. It was more soluble in ethyl and amyl alcohol than in water. A cold, aqueous solution of the acid was unaffected by addition of ferric chloride solution, while the solution on warming turned brown. When heated in a capillary tube, the substance did not melt, but underwent partial decomposition when heated above 200° . Nitrogen and sulfur determinations agreed with the calculated values for the isodithiocyanic acid. For the purposes of identification this acid was synthesized in accordance with given directions.¹ The two compounds proved to be identical in every respect. We did not obtain any evidence of the formation of acetylpersulfocyanic acid or acetylthiourea.

Calc. for $C_2H_2N_2S_2$: N, 23.77; S, 54.24. Found: N, 23.88, 23.93; S, 53.86.

The above experiment was also carried out under somewhat altered conditions. The heating period was shortened to one hour and the reaction mixture then poured into cold water. A granular precipitate formed immediately. It weighed 2.4 g. and proved to be isodithiocyanic acid. The yield, therefore, was practically the same as in the first experiment.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]
**RESEARCHES ON HYDANTOINS. XXXV. A NEW METHOD OF
SYNTHESIZING GLYCOCYAMIDINE COMPOUNDS, AND
THE CONVERSION OF GLYCOCYAMIDINE
INTO ISOMERS OF CREATININE.**

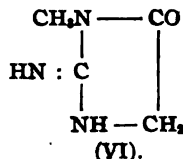
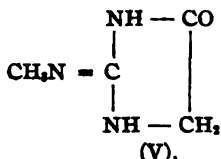
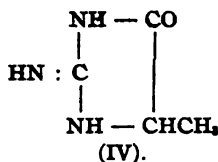
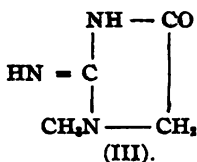
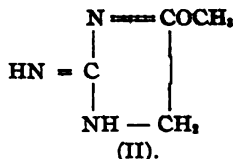
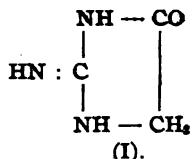
BY TREAT B. JOHNSON AND BEN H. NICOLET.

Received July 31, 1915.

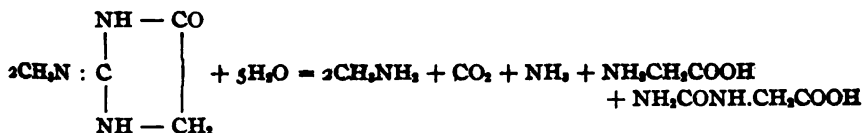
If we disregard amidine and keto-enol tautomerism, there are only five structurally isomeric monomethyl derivatives of glycocyamidine (I) theoretically possible. Three of these are nitrogen substituted com-

¹ *Ann.*, 179, 204 (1875).

pounds represented by Formulas III (creatinine), V and VI. One is a carbon derivative or the long known alacreatinine¹ (IV), and the last an oxygen derivative corresponding to Formula II. All five isomers would be basic compounds. Previous to 1904 only two of these isomers had been described, namely, creatinine (III) and alacreatinine (IV).



During this year Korndörfer,² who worked under the direction of E. Schmidt, published a paper entitled "Untersuchungen über das Glycocyamin und das Glycocyamidin," in which he described the behavior of glycocyamidine towards methyl iodide. He observed that the cycle underwent alkylation smoothly, forming the hydriodic acid salt of a new base to which he assigned Formula V and named it α -methylglycocyamidine. Creatinine (III) was represented by him as the β -derivative, and alacreatinine (IV) as the γ -derivative of glycocyamidine. The evidence on which Korndörfer established the constitution of this glycocyamidine derivative was the fact that it underwent hydrolysis when heated with barium hydroxide solution, with formation of ammonia, methylamine, glycocoll and hydantoic acid. The reaction may be expressed as follows:



Six years after the appearance of this work a second paper, under the same title, was published by M. Schenck,³ in which this investigator

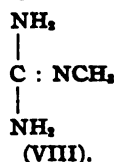
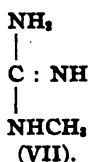
¹ *Ann.*, 167, 83; *Ber.*, 6, 1371 (1873).

² *Archiv. Pharm.*, 242, 620 (1904).

³ *Ibid.*, 248, 376 (1910).

refers to the previous work of Korndörfer¹ on α -methylglycocyanidine, and calls attention to the fact that Formula VI could be assigned to his alkylation products as well as V, since both compounds would give the same decomposition products on hydrolysis with alkali. Schenck, therefore, sought to determine the constitution of Korndörfer's methylglycocyanidine and distinguish between the two modifications (V) and (VI) by oxidation with potassium permanganate. He wrote as follows:

"Eine Entscheidung zwischen den beiden obigen Formeln (V und VI) konnte sich durch die Oxydation mit Kaliumpermanganat treffen lassen, indem ein Methylglykocyanidin der letzteren Art dasselbe Methylguanidin liefern müsste, wie das Kreatinin, während ein Methylglykocyanidin der Korndörfer'schen Formel hierbei das bisher unbekannte Methylguanidine (VIII) ergeben sollte."



Schenck oxidized his methylglycocyanidine according to the method used by Neubauer² in his work on creatinine and obtained a *methylguanidine*, which proved to be identical, as might be expected, with that obtained by oxidation of creatinine,³ and also that formed by addition of methylamine to cyanamide. Schenck considered this result sufficient proof of the structure of the methylglycocyanidine and concluded as follows:

"Demnach muss man die von Korndörfer angenommene α -Formel V des Methylglykocyanidins aufgeben und die γ -Formel VI annehmen."

No further papers were contributed on this subject until that of E. Schmidt,⁴ entitled "Ueber das Kreatinin," appeared during the same year. He reviewed the work of Korndörfer and Schenck, emphasizing the significance of Schenck's speculations, and stated that an investigation dealing with the synthesis of the unknown α -methylglycocyanidine was in progress. So far as we are aware, no report has been made of the work. His students, Kunze⁵ and Henzerling,⁶ investigated the behavior of creatinine on alkylation and obtained, by the action of methyl iodide and ethyl iodide, methyl- and ethylcreatinines to which they assigned Formulas IX and X, respectively. They state that both compounds underwent oxidation with potassium permanganate, forming symmetric dimethylguanidine (XI) and *sym*-methylethylguanidine (XII), respectively.

¹ *Loc. cit.*

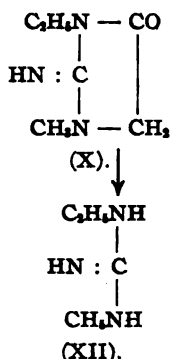
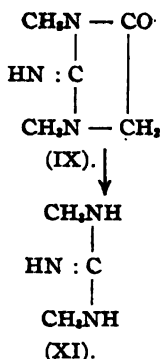
² *Ann.*, 119, 46 (1861).

³ Neubauer, *loc. cit.*

⁴ *Archiv. Pharm.*, 248, 568 (1910).

⁵ *Ibid.*, 248, 578 (1910).

⁶ *Ibid.*, 248, 604 (1910).



In our opinion, Schenck's procedure of oxidizing monoalkylated glycoyamidines with potassium permanganate is of no more value for proving the constitution of such compounds than that employed by Korndörfer,¹ namely, hydrolysis of the glycoyamidine with alkali. We have available no means of deciding positively the location of the double bond in a monoalkylated guanidine (VII) or (VIII) or a symmetrically substituted dialkylguanidine (XI) or (XII). Of the three isomeric methylglycoyamidines (III), (V) and (VI), all would undergo oxidation with potassium permanganate with formation of methylguanidine (VII) or (VIII), while creatinine (III) can easily be distinguished from the isomers (V) and (VI) by hydrolysis with alkali. It is converted into sarcosine while the isomers (V) and (VI) would break down with formation of glycoll and methylamine.

Schenck² later realized the weakness of his speculations and endeavored to synthesize tautomeric modifications of mono- and dialkylated guanidines. All his attempts, however, to prepare such isomers, as might be expected, were unsuccessful.

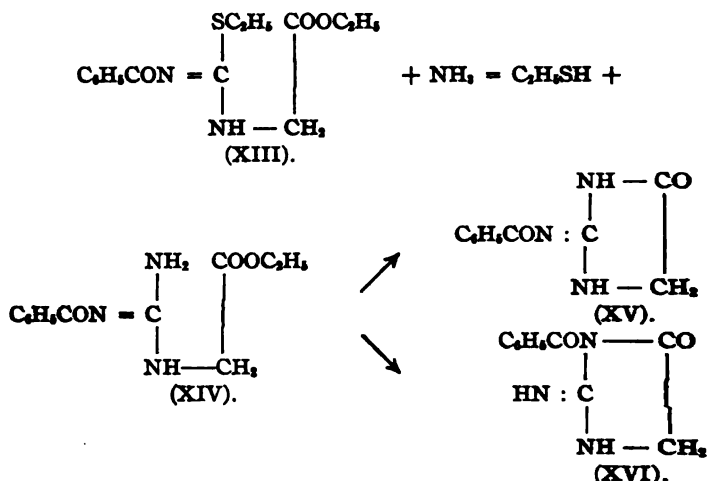
We have now developed a new method whereby glycoyamidine and its alkylated derivatives can be prepared very easily. We find that such combinations can be synthesized by the action of amines on the ethyl ester of benzoylpseudoethylthio-hydantoic acid (XIII). The latter compound has been described in a previous paper³ from this laboratory, and is obtained by the interaction of ethyl aminoacetate with diethyl benzoylimidodithiocarbonate. When the ester is allowed to interact with an amine, mercaptan is evolved and a substituted guanidine (XIV) is formed. This then condenses to form a glycoyamidine with loss of a molecule of alcohol. Two isomeric glycoyamidines (XV) and (XVI) can theoretically be formed in such a change, depending on which nitrogen

¹ *Loc. cit.*

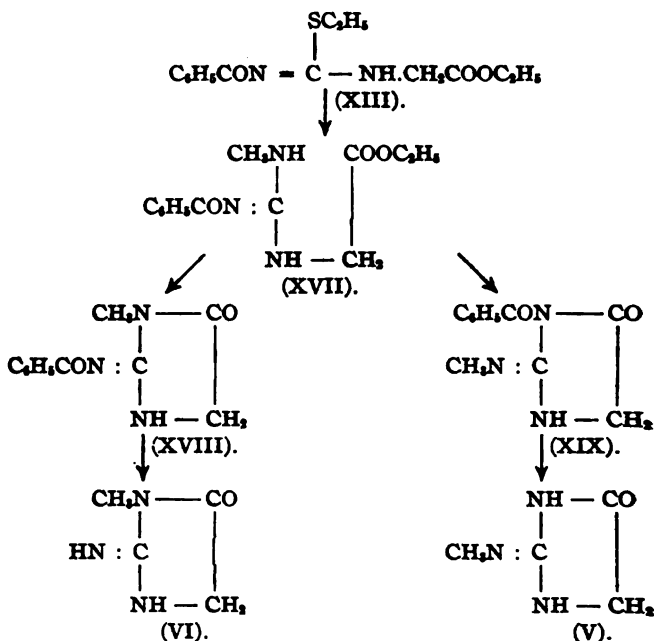
² *Z. physiol. Chem.*, **77**, 328 (1912); *Arch. Pharm.*, **249**, 463 (1911); *Chem. Centr.*, **2**, 1216 (1911).

³ Wheeler, Nicolet and Johnson, *Am. Chem. J.*, **46**, 456 (1911).

of the guanidine is incorporated in the ring. Ammonia reacted according to the following expression to form 2-benzoylglycocyamidine (XV).



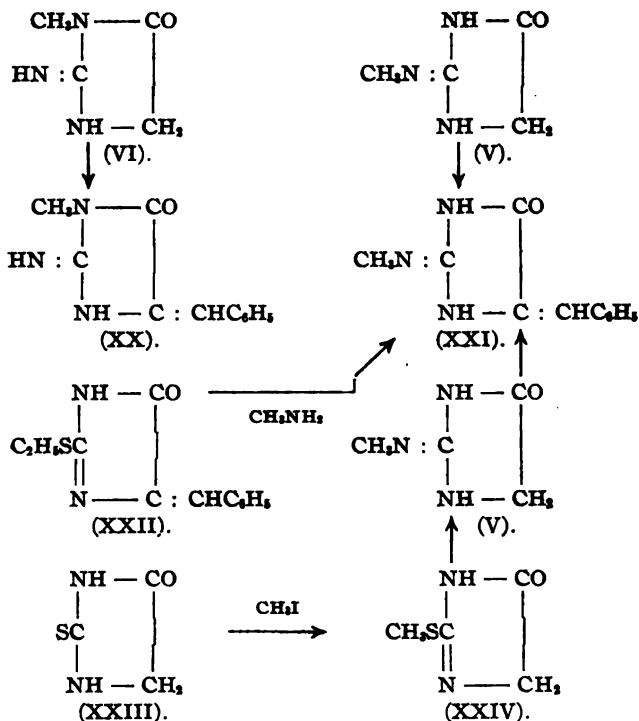
With methylamine we obtained the guanidine derivative represented by Formula XVII, which then underwent a molecular condensation with formation of the two possible glycoyamidines (XVIII) and (XIX). About 85% of the guanidine (XVII) condensed to form 1-methylbenzoylglycocyamidine (XVIII), while the remainder was transformed



into the 1-benzoyl-2-methylglycocyanidine (XIX). The isomers were hydrolyzed by warming with hydrochloric acid and converted into the corresponding hydrochlorides of α -methyl- and γ -methylglycocyanidines, represented by Formulas VI and V, respectively. The changes may be expressed as above.

The hydrochloride of α -methylglycocyanidine (V) was not isolated. A description of the hydrochloride of the isomeric glycocyanidine (VI), which was identical with Korndörfer's salt, is given in the experimental part of this paper.

That two isomeric methylglycocyanidines (V) and (VI) were formed in this reaction was established in the following manner: The crude glycocyanidine formed by hydrolysis was digested with benzaldehyde and sodium acetate, in acetic acid, when it interacted to form the two benzal derivatives represented by Formulas XX and XXI. These two compounds are characterized by their difference in behavior towards alkali. The glycocyanidine (XX) is insoluble in dilute alkali, while its isomer (XXI) is an acid ($-\text{CO.NH}-$ grouping) and dissolves at once. In this manner, therefore, the isomers can be separated easily and the soluble form (XXI) obtained in a pure condition by precipitation from its alkaline solution with acid. The relative proportion of the two isomers in a mix-



ture can be determined very accurately by this method. That the benzalglycocycamidine soluble in alkali is a 2-methyl derivative (XXI) was established by its synthesis by two other methods. The same compound was obtained by heating 2-ethylmercapto-4-benzal-5-ketodihydroimidazole¹ (XXII) with methylamine, and also from 2-thiohydantoin (XXIII) in the following manner: This was first converted into its methylmercapto derivative (XXIV) by alkylation with methyl iodide and this then into the 2-methylglycocycamidine (V) by heating with methylamine. This hitherto unknown glycocycamidine was condensed with benzaldehyde when the corresponding benzal derivative (XXI) was obtained in good yield (55%).

These aldehyde condensation products should prove to be of general usefulness to biochemists for isolating glycocycamidine compounds and determining the constitution of alkylation products of this type. Hitherto, the characteristic derivatives, which have been of service for the isolation and identification of such compounds, have been the picrates and gold and platinum double salts. Some give characteristic precipitates with inorganic salts (ZnCl_2). The benzal compounds are difficultly soluble, possess high melting points and are very stable in the presence of dilute alkali. The study of glycocycamidine compounds will be continued.

Experimental Part.

2-Benzoylglycocycamidine (XV).—Ethyl benzoylpseudoethylthiohydantolate,² $\text{C}_6\text{H}_5\text{CON}:\text{C}(\text{SC}_2\text{H}_5)\text{NH}\cdot\text{CH}_2\text{COOC}_2\text{H}_5$, was dissolved in alcohol and 1.5 molecular proportions of ammonia in aqueous solution added. Ethyl mercaptan was evolved slowly. The mixture was allowed to stand for 5 days and finally heated on the steam bath for one-half hour to complete the reaction. After concentration of the solution and cooling, the glycocycamidine was obtained in the form of colorless needles. The compound is moderately soluble in hot alcohol and difficultly soluble in cold. It has no definite melting point but blackens and decomposes when heated to 230° . Analysis:

Calc. for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}_3$: N, 20.6. Found: N, 20.38.

The Action of Methylamine on Ethyl Benzoylpseudoethylthiohydantolate with Formation of 1-Methyl-2-benzoylglycocycamidine (XVIII) and 1-Benzoyl-2-methylglycocycamidine (XIX).—The ethylthiohydantolate was covered with its own weight of alcohol, and somewhat more than the calculated amount of methylamine, in 33% aqueous solution, then added. Ethyl mercaptan was evolved immediately at ordinary temperature. The mixture was allowed to stand in a tightly stoppered flask for 24 hours and then heated to boiling for one-half hour. On cooling the glycocycamidine (XVIII) separated in the form of distorted needles which melted at 214° . The compound was readily soluble in hot alcohol, mod-

¹ Johnson and Nicolet, *THIS JOURNAL*, **34**, 1048 (1912).

² Wheeler, Nicolet and Johnson, *loc. cit.*

erately soluble in cold and very soluble in hot water. The yield was excellent, being about 85% of the theoretical. Analysis:

Calc. for $C_{12}H_{11}O_2N_3$: N, 15.95. Calc. for $C_{11}H_{11}O_2N_3$: N, 19.30. Found: N, 19.12.

1-Benzoyl-2-methylglycocycamidine (XIX) was also a product of this reaction, but it was not isolated. The experimental evidence, which indicates its formation, is given below.

Hydrochloride of 1-Methylglycocycamidine (VI).—The 1-methyl-2-benzoylglycocycamidine (benzoylisocreatinine) described above was dissolved in alcohol and digested for 8–10 hours on the steam bath with an excess of concentrated hydrochloric acid. The solution was then evaporated to dryness and the residue triturated with a small amount of cold water. This dissolved completely the glycocycamidine hydrochloride and left behind the benzoic acid. After filtering, this aqueous solution of the hydrochloride was evaporated to dryness and the salt dissolved in the smallest possible volume of 95% alcohol and this solution diluted with ether. The hydrochloride of methylglycocycamidine separated at once and the yield corresponded to about 75% of the calculated amount. The salt crystallized in characteristic granular crystals. When heated in a capillary tube, the salt began to change in appearance at 200°, blackened badly above 250° and at about 283–285° decomposed with strong effervescence. It is very soluble in hot water and alcohol, and practically insoluble in ether. It is easily purified by dissolving in fresh alcohol and then reprecipitating by addition of ether.

Calc. for $C_8H_9ON_2Cl$: N, 28.0. Found: N, 27.60.

This salt agreed in all its properties, so far as we were able to judge, with that described by Korndörfer.¹ It combined with picric acid, giving an insoluble picrate, which separated in short prisms melting at 196° when heated slowly. Korndörfer gives 193° as the melting point. The chloraurate deposited as short, yellow prisms which melted at 166° with slight effervescence. Korndörfer gives 168° as the melting point of his salt. Our salt (HCl) gave in aqueous solution the same color reactions, described by Korndörfer, with sodium nitroprusside, picric acid and Fehling's solution.

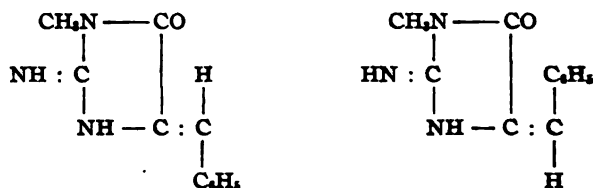
Condensation of Benzaldehyde with a Mixture of 1-Methylglycocycamidine and 2-Methylglycocycamidine.—In this experiment we used 3 g. of the crude hydrochloride of 1-methylglycocycamidine, which was prepared by hydrolysis of the corresponding benzoyl derivative (XVIII) and (XIX) described above. The crude hydrochloride, one molecular proportion of benzaldehyde, three molecular proportions of anhydrous sodium acetate and 20 cc. of glacial acetic acid were heated to boiling, in an oil bath, for one hour. After cooling and diluting with water 3.35

¹ *Loc. cit.*

g. of the condensation product were obtained. This reaction product was not a definite substance, although after crystallization from alcohol it melted quite sharply at 219–220°. When it was triturated with cold 5% sodium hydroxide solution (it is necessary that this alkali be kept cold in order to avoid all hydrolysis), the greater part remained undissolved and was identified as *1-methyl-4-benzalglycocycamidine* (XX). This new compound crystallizes from alcohol in flat, orange-colored prisms which melt at 246–247° with violent effervescence. It is slightly soluble in hot water and insoluble in cold.

Calc. for $C_{11}H_{11}ON_2$: N, 20.86. Found: N, 20.94.

Mixed with this hydantoin there was always obtained a small amount of material which crystallized from alcohol in needles melting at 237–239°. This compound also was insoluble in hot 5% potassium hydroxide solution. It contained the same percentage of nitrogen as the above benzal derivative (Found: N, 20.7). Owing, however, to the extremely small quantity obtained, its constitution could not be established, but it was very probably a stereoisomeric modification of *1-methyl-4-benzalglycocycamidine*. Such a relationship would be expressed by the following formulas:



That combinations of this type (hydantoins) can exist in isomeric forms has already been shown by Johnson and Hadley¹ and also Johnson and Bates.

The sodium hydroxide solution (see above) was acidified with acetic acid, when a crystalline substance separated at once. This was purified by crystallization from alcohol and separated as needle-like prisms, which melted at 223° to a clear oil. It was identified as *2-methyl-4-benzalglycocycamidine* (see below). A mixture of this compound with its isomer melting at 246–247°, melted at 210°. In other words, the original *methylglycocycamidine hydrochloride*, which was used in this condensation was a mixture of two salts, namely, *1-methylglycocycamidine* and *2-methylglycocycamidine hydrochlorides*. The chief proportion of the salt was the *1-methyl* derivative.

2-Methyl-4-benzalglycocycamidine (XXI).—For the purpose of identification this glycocycamidine derivative was synthesized by two different methods. It was prepared from 2-ethylmercapto-4-benzalhydantoin

¹ THIS JOURNAL, 37, 171 (1915).

² *Ibid.*, 37, 383 (1915).

as follows: The hydantoin was dissolved in an alcoholic solution of methylamine and this heated in a bomb tube. After heating for six hours at 100° there was no odor of ethylmercaptan and the mercaptohydantoin was recovered unaltered. Only a trace of ethylmercaptan was noticeable after heating again for 3 hours at 155–160°. When heated at 200° mercaptan was not only evolved, but the compound had apparently undergone complete decomposition and no definite crystalline substance could be isolated. A partial change of the mercaptohydantoin into the 2-methylamino derivative was finally effected by heating for 36 hours at 100°. Under these conditions about one-fifth of the mercapto compound had undergone the desired change and the benzalglycocycyamidine was obtained in the form of needles which melted at 222°. The substance was readily soluble in dilute alkali (—CO.NH— group) and was reprecipitated by acids. The yield was poor. A mixture of this material with some of the product obtained in the previous experiment (melting at 223°) melted at 221°. They were apparently identical (Found: N, 20.4%).

This same glycocycyamidine compound was also obtained in the following manner: Three grams of 2-thiohydantoin¹ were alkylated with methyl-iodide in dilute alcohol solution and in the presence of alkali and converted into the corresponding methyl-mercapto derivative² (XXIV). The resulting solution was then concentrated to a volume of about 20 cc. and heated for 6 hours at 100° with an excess of methylamine. Ethylmercaptan was evolved and the corresponding 2-methylglycocycyamidine was formed. The reaction, however, is not a smooth one and we always obtained here a purple, tarry product on evaporating, from which it was practically impossible to isolate the glycocycyamidine. Therefore, in order to establish its presence the reaction mixture was concentrated as much as possible by heating on the steam bath and the residue dissolved in glacial acetic acid. Approximately the required amount of benzaldehyde and an excess of anhydrous sodium acetate were then added and the mixture boiled for 3 hours. On pouring this mixture into water, 2-methyl-4-benzalglycocycyamidine separated at once. The yield was about 55% of the theoretical. The glycocycyamidine dissolved completely in alkaline solutions and crystallized from alcohol in prismatic crystals which melted at 223°. This melting point was not lowered by mixing with this product some of the glycocycyamidine obtained by the action of methylamine on 2-ethylmercapto-4-benzalhydantoin.

4-Benzalglycocycyamidine.—This compound has previously been described by Ruhemann and Stapleton.³ We obtained the same compound

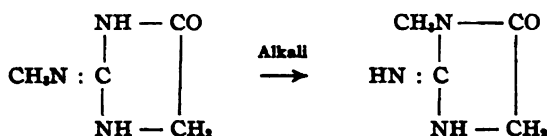
¹ Johnson and Nicolet, *loc. cit.*

² Komatsu, *Memoirs Coll. Sci. and Eng. Kyoto Univ.*, 3, 7 (1911).

³ *J. Chem. Soc.*, 77, 239 (1900).

by condensing glycoxyamidine with benzaldehyde in glacial acetic acid and in the presence of sodium acetate. It was purified by crystallization from alcohol and separated as a crystalline powder which melted at 297°. Ruhemann and Stapleton assigned to their compound a melting point of 295°. This compound undergoes alkylation with substitution in the 1-position of the ring. It reacted with methyl iodide in the presence of potassium hydroxide forming 1-methyl-4-benzalglycoxyamidine. This was insoluble in dilute alkali and melted at 246°. We obtained no evidence of the formation of 2-methyl-4-benzalglycoxyamidine melting at 223°.

The Molecular Rearrangement of 2-Methylglycoxyamidine into 1-Methylglycoxyamidine.—Two grams of 2-thiohydantoin were alkylated



with methyl iodide and converted into the corresponding 2-methyl-mercapto derivative (XXIV) as described above. The mercapto group was then removed by heating with methylamine as already described. After the reaction was complete the solution of methylglycoxyamidine was then concentrated to a small volume, diluted with 20 cc. of 5% potassium hydroxide solution, and the mixture then warmed on the steam bath for 10 minutes. The solution was then made strongly acid with an excess of hydrochloric acid and finally digested on the steam bath for 8 hours. After this treatment, the solution was concentrated, as far as possible, by heating at 100° and the residue then condensed with benzaldehyde by heating in glacial acetic acid solution in the presence of sodium acetate. On pouring into water, we obtained, as usual, the condensation product. This was triturated with 5% potassium hydroxide solution when only about 30% of it dissolved, leaving behind a crystalline residue which was identified as 1-methyl-4-benzalglycoxyamidine. It melted at 246°. When the alkaline solution was acidified with hydrochloric acid the isomeric 2-methyl-4-benzalglycoxyamidine melting at 222° was obtained. In other words, 2-methylglycoxyamidine undergoes hydrolysis with alkali and is transformed into its corresponding glycoxyamine. This is closed by action of acid forming the original 1-methylglycoxyamidine and also some 2-methylglycoxyamidine. It is apparent from these results that, in the alkylation of glycoxyamidines in the presence of alkali, different alkylation products can be formed, depending on the conditions employed.

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

ON THE DIGESTIVE ACTIVITY AND COMPOSITION OF DIFFERENT FRACTIONS OF THE PANCREAS. I.

BY J. H. LONG, MARY HULL AND H. V. ATKINSON.

Received July 31, 1915.

In a recent paper by one of us and Fenger,¹ it was shown that by the aid of the centrifuge it is possible to effect a mechanical separation of minced pancreas tissue in such a manner as to secure three layers of products in the centrifuge tubes possessing different properties. For this purpose we have employed a large laboratory centrifuge made by the International Instrument Company having eight tubes holding about 75 cc. each. These, or usually four of them, have been filled with the finely minced pancreas and rotated at a speed running up to 3500 revolutions per minute, through 45 minutes. The ordinary speed was about 3000 revolutions, because at the highest speed there is too great an elevation of temperature, which should be avoided.

By this centrifugal action the minced mass gradually separates into three layers. In the bottom of the tube we have an excess of protein substance more compact than the original minced gland. Above it there is a liquid layer which is distinct and nearly clear. Filtration is easy and the filtrate is perfectly bright. The top layer is composed of fat and a smaller amount of protein usually, with some water of course, as the separation of the latter is never complete. How far this might be effected by a higher velocity of rotation we do not know, but doubtless to a marked degree. The relative weights of these layers varies to a considerable extent with the speed and time of revolution, but in the majority of the mixed glands examined by us the lower layer made up 50%, or more, of the whole. In some cases the liquid and top layers were about 25% each.

To separate these three layers it is best to chill the tubes and contents. The fatty layer may then be removed with a spatula and the liquid layer poured off through a filter which makes it perfectly clear.

Separate examinations were made of the three layers, the results of which are given in the tables below. Most of the figures explain themselves, but for the starch digestion this must be said: The digesting power is measured by the number of parts of starch, employed in the form of a 1% paste, which may be digested to the colorless end point in 10 minutes, by one part by weight of the ferment mass. Thus, 1 cc. of the liquid in Col. B of the first table will digest 154 g. of starch, calculated as anhydrous, to the point where it will give no reaction with iodine after the mixture has been incubated 10 minutes at a temperature of 40°.

In the fibrin digestion the values given refer to the number of milligrams of amino nitrogen, as measured by the formaldehyde titration,

¹ THIS JOURNAL, 37, 2213 (1915).

liberated by one gram or cubic centimeter of the substance, when allowed to act on an excess of fibrin and incubated through 18 hours at 37°. The numbers have been corrected by subtracting the results of blank titrations where killed ferments were employed.

No attempts were made to compare the three fractions as to their lipase activity, but qualitative tests showed the liquid fractions markedly active in esterase.

In such centrifuge fractionations as we are concerned with here, some variation in the relative quantities of the layers is found. In most cases we obtained a better separation from the beef than from the hog or sheep pancreas. With pancreases from old sheep the separation seems to be difficult. In the tables below the means from four tests on hog pancreas, three tests on beef pancreas and from a number of partial tests on sheep pancreas are given. In this last case the numbers are therefore somewhat misleading. The letters A, B and C at the top of the columns refer to the upper, middle and lower layers, respectively.

TABLE I.

	Hog pancreas fractions.			Beef pancreas fractions.		
	A.	B.	C.	A.	B.	C.
Approx. wt., % of whole	36.3	17.2	46.0	16.0	23.4	60.6
Solids, % of fraction....	49.3	15.0	31.2	60.0	11.4	29.6
Fat, % of fraction.....	34.0	6.8	50.7	8.3
Phosphorus, % of fat...	0.27	0.27	0.26	0.27
Phosphorus, % of fraction	0.37	0.46	0.47	0.30	0.47	0.50
Nitrogen, % of fraction	1.49	2.22	3.42	1.16	1.87	2.95
PH.....	5.54 ¹	5.537
F. p. depression.....	1.62°	1.12
Starch digestion.....	0.44	1.54	1.78	0.12	0.82	0.49
Fibrin digestion, amino N	0.029	0.017	0.036	0.016	0.015	0.029
	Sheep pancreas fractions.					
	A.	B.	C.			
Approx. wt., % of whole.....	3.2	12.5	84.3			
Solids, % of fraction.....	(90.0)	14.2	26.4			
Fat, % of fraction.....	(85.0)	4.5			
Phosphorus, % of fat.....	0.29			
Phosphorus, % of fraction.....	0.40	0.51			
Nitrogen, % of fraction.....	0.19	1.88	3.02			
PH.....	5.7			
F. p. depression.....	1.13			
Starch digestion.....	1 : 0.08	1 : 0.17	1 : 0.25			
Fibrin digestion, amino N.....	0.013	0.019			

The table shows some points of interest. With equal periods of rotation in the centrifuge it is evident that a much larger weight is secured in the upper fraction in the case of the hog than is true of the other animals. But the sheep pancreases used for these first tests were from old animals and different results may be secured in later tests with the organs of

younger animals. Fat is found in both the upper and lower layers, but much more in the former. The phosphorus content of all the fats is essentially the same and suggests a uniform composition. The amount is always low and this shows that the lipoid fraction present can not be over 7 or 8%, in any case, of the weight of the fat. The amount of phosphorus in the common distearyl lecithin is about 3.9%. It should be explained here that in all cases the fatty tissue attached to the pancreas was trimmed away as far as possible before grinding, so that the fat found is largely that in the organ itself.

It is plain that the amylopsin passes to a great extent into the liquid fraction, where it is especially abundant in the case of the hog. The four individual tests, pancreases of different dates, from which the mean was taken, gave the values, 156, 180, 156 and 125, and even these do not represent the maximum digesting power, since, as is well known, solutions of the ferment in question rapidly lose digesting activity on standing. The value 125 was obtained from a liquid which had stood about six hours before tests could be made with it.

This starch converting ferment is low in the fatty layer in all cases and it is interesting to note that it is abundant only in the pancreas of the hog. This fact is practically utilized by the manufacturers of the pancreatins of the market, but the discrepancy is not always as great as is here indicated.

In tryptic power the fractions all appear low, but the greatest activity is found in the bottom layer in all cases, and the lowest in the liquid. This is doubtless connected with the fact that trypsin tends to attach itself to proteins, and especially to suspended proteins. It is not clear just what degree of activity is indicated by the figures presented. The liberation of amino nitrogen has evidently not gone very far in any case. But the liquid fractions were always tested as to their action on flakes of fibrin and a digesting power noted in every instance. All of these tryptic digestions were carried out in a phosphate medium of which $P_H = 7.73$, which is but slightly alkaline and constant in reaction. The important point in this connection is, however, that through crushing of the pancreas cells the trypsinogen becomes activated by the coferment present in the tissue and exhibits its power at once. In a following paper more attention will be given to the extent of this tryptic action and also to the behavior of the lipase and esterase. The data here presented must be looked upon as preliminary to the discussion of the ferments in the fractions.

Attention must be called to the importance of the acid reaction found in this pancreas fluid of the third fraction in all the animals. The data on this point are more fully presented elsewhere¹ but it must be noted that, while in all laboratory digestions with amylopsin and trypsin the

¹ Long and Fenger, *Loc. cit.*

preferable reaction for activity is found to be slightly alkaline, the fluid itself in which the ferments are elaborated is distinctly acid. It seems to be true, in addition, that the stability of both ferments is greatest in the presence of weak acid. The degree of acidity of the fluid was found to be nearly the same for the three animals investigated, but there are doubtless fluctuations here, as in the blood, which call for fuller investigation later.

Our thanks are due to Dr. Frederic Fenger for his courtesy in aiding us in securing the pancreases, to Mr. William Johnson for the determinations of the starch-converting power and to Professor A. I. Kendall for the use of the centrifuge of the bacteriological laboratory.

Conclusions.

We have explained the method of separating a minced organ like the pancreas into three fractions by the aid of a powerful centrifuge. In the case of the pancreas these fractions have different properties, especially with reference to the distribution and amount of the ferments present. The general composition of the three fractions for the organ of the hog, beef and sheep is given. It is likely that the method can be applied with advantage to the study of the fluids contained in other tissues, and especially to the enzymes present.

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THE NEPHELOMETRIC ESTIMATION OF PURINE BASES, INCLUDING URIC ACID, IN URINE AND BLOOD.¹

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Received July 10, 1915.

CONTENTS: I. Introduction, II. Method: *A*. Precipitant; 1. Reagent, 2. Protective Colloid, 3. Use of Precipitant, *B*. Separation of Uric Acid from Purine Bases, III. Directions, IV. Applications; *A*. Urine, *B*. Blood, V. Summary.

I. Introduction.

The estimation of purine bases with the exception of uric acid, is at present a long and often inaccurate process. Recently Folin² and collaborators have developed a colorimetric reagent for uric acid, which does not react with the other purines, but gives reactions with phenols and allied substances. To circumvent the difficulty they precipitated the uric acid with Salkowski's reagent and, after washing by decantation, make the colorimetric estimation. This method is sensitive to small amounts of uric acid but the present methods for determining the other purine bases, xanthine, hypoxanthine, adenine and guanine require such large

¹ Read before the Am. Soc. Biol. Chem., Dec., 1914, St. Louis, Mo.

² Folin and Macallum, *J. Biol. Chem.*, 13, 363 (1912); Folin and Denis, *Ibid.*, 14, 95 (1913)

amounts of material as to make them unsuitable for blood analysis and their estimation in urine consumes the better part of two days.

While developing technic for the determination of guanine and adenine in the study of nucleases along nephelometric lines,¹ it was found possible to estimate both uric acid and other purines in a few minutes. The requirements for such a method were (1) a nephelometric precipitant² for these substances and (2) a means of eliminating either uric acid or the other purines from reacting with this precipitant.

II. Method.

A. Precipitant.—The reagents used now, ammoniacal silver nitrate and magnesium mixture in Salkowski's method, and cupric sulfate with sodium hyposulfite in the Krüger-Schmidt method, have heretofore been considered specific. The difficulties of these methods were therefore not in the precipitation but in the subsequent isolation or analysis of the purine bases after precipitation. As colors are developed with the Krüger-Schmidt reagents, no attempt was made to apply them nephelometrically, attention being confined to Salkowski's reagent.

(1) **Reagent.**—Salkowski's reagent consists of equal volumes of magnesia mixture and ammoniacal silver nitrate (26.0 g. in 1 liter and sufficient NH_3 to prevent precipitation of AgO). Ammoniacal silver nitrate precipitates the purine bases as a white silver complex, but black reduced silver is formed with uric acid, unless chlorides are present.

After careful study of pure material, uric acid,³ xanthine,⁴ hypoxanthine,⁵ guanine,⁶ and adenine,⁷ separately or in mixtures, it was found necessary to modify the reagent as follows:

(a) The concentration of the silver nitrate was reduced.

(b) Ammonium chloride alone was found more suitable than magnesium mixture.

(c) The amount of ammonium hydroxide had to be redetermined.

In 100 cc. of reagent, silver nitrate was varied from 10 to 50 cc., magnesia mixture from 0.5 to 50 cc. (0.5 cc. being the smallest amount which would prevent the reduction of silver upon adding uric acid) and the ex-

¹ Kober and Graves, "Nephelometry in the Study of Nucleases," *THIS JOURNAL*, 36, 1304 (1914).

² For the definition of "Nephelometric Precipitant" see *THIS JOURNAL*, 35, 1585 (1913).

³ Kahlbaum's.

⁴ Merck's.

⁵ Prepared in this laboratory from beef extract.

⁶ Prepared in this laboratory from yeast nucleic acid according to Walter Jones whose directions, given in his "Monograph on Nucleic Acids," were found complete in every respect, and very satisfactory results were obtained.

⁷ Also from yeast nucleic acid according to Jones. We received from Dr. P. A. Levene, of Rockefeller Institute, sufficient adenine picrate to make our preliminary experiments, for which we wish to express our thanks.

cess of ammonium hydroxide was varied from 2 to 12 cc. It was found that the uric-acid-silver complex was somewhat soluble in a large excess of ammonia, but some excess was necessary to prevent the formation of any insoluble silver chloride and to allow for ammonia evaporation while making the readings. The difficulty with the magnesia mixture was the formation, upon standing with an excess of ammonium hydroxide, of a white precipitate, possibly magnesium hydroxide and silver either in combination or occluded, which interfered with the work unless the solution was allowed to stand over night and filtered. This trouble was obviated by using ammonium chloride, only. Ammonium chloride solution was varied from 1 to 8 cc. per 100 cc. The reagent finally adopted as suitable for the precipitation of purines for nephelometric estimation consists of:

Fifty cc. of ammoniacal silver nitrate solution¹ (26.0 g. in a liter, with sufficient ammonium hydroxide—26 to 27 cc. s. g. 0.90—to prevent AgO from settling out).

Eight cc. of ammonium chloride solution (containing 16.5 g. in 100 cc.).

Sufficient ammonium hydroxide to redissolve any silver chloride formed, usually 9 cc. of s. g. 0.90.

An excess of 5 cc. of ammonium hydroxide of s. g. 0.90, and then sufficient water to make 100 cc. volume.

This reagent, if kept in well stoppered bottles, keeps indefinitely.

(2) **Protective Colloid.**—While the reagent was being worked out it was found that suspensions formed with dilute solutions of the purine bases either flocculated at once (uric acid and adenine), or in very few minutes (xanthine, hypoxanthine and guanine). It was therefore necessary to find a medium in which these precipitates remained in suspension long enough for making readings (7 to 30 minutes). In other words a protective colloid was sought which would hold the substances in suspension. After trying Witte's peptone, gelatin, soluble starch and casein, egg albumin in dilute solution was found to serve the purpose satisfactorily.

We know of no previous work in which protective colloids have proved an aid rather than a hindrance in quantitative analysis.

Albumin.²—From work with albumin, as a precipitant for nucleic acids, it was assumed that fresh egg white would have the strongest protective action, but the reverse proved true and after experiments with eggs of varying age, it was proven that albumin from eggs several months old (cold-storage eggs) was a stronger protective colloid than albumin from fresh eggs. That old eggs have a stronger protective action is probably

¹ It is best to filter the ammoniacal silver nitrate solution before using from traces of reduced silver or filter the reagent finally.

² Commercially dried egg albumins were dried in a few experiments but seemed unsatisfactory.

due to the action of ferments. The incubation of fresh eggs improved their protective action, but the results were not as good as with eggs which had been some months in storage. For example, fresh egg albumin in the form of a 2.0% solution kept uric acid in suspension for 4-6 minutes, while fresh eggs that had been incubated at 40° for 4 days were efficient for about 18 minutes, and storage eggs prevented agglutination for more than 60 minutes. Eggs that had been in storage for a number of weeks were very much improved by three to four days' incubation. Longer incubation did no harm, except that it made the separation of the yolk from the white more difficult. Care must be taken to keep the yolk out of the albumin to be used, as much of it tends to produce cloudy solutions.

The isolation and purification of the active principle in egg white both for this purpose, and for use as a precipitant with nucleic acids would be a further advantage in the methods.

A weighed amount of egg white¹ was well shaken with 0.1 *N* acetic acid (0.5 cc. per gram. of egg white²) and sufficient water was added to make a 2.0% albumin solution, the egg white being calculated as containing 10% of albumin. The solution was then thoroughly mixed and filtered until clear.

The protective action of this albumin solution varied with particular purines and mixtures of purines. Table I give the strength of albumin most suitable in each case and the time before flocculation takes place.

TABLE I.

Substance.	Albumin. %.	Time before flocculation. Min.	Mixtures of equal parts of	Albumin. %.	Time before flocculation. Min.
Uric acid.....	2.0	30+	Xanthine	0.0	20+
Xanthine.....	0.5	15+	Hypoxanthine		
Hypoxanthine.....	0.05	10	Guanine		
Guanine.....	0.05	20+	Adenine	0.3	30+
Adenine.....	2.0	8	Xanthine		
			Hypoxanthine		
			Adenine	0.07	30+
			Guanine		

Ten cc. 0.01% solution of the purine bases or mixture were used in each instance, with the exception of adenine sulfate, which in that strength gave too strong a precipitate to be held in suspension by 2.0% albumin. Adenine sulfate standard solutions were therefore only 0.005%. To 10 cc. of the solution were always added 10 cc. of the correct albumin solution and 10 cc. of the reagent. It is to be noted that mixtures as a rule re-

¹ For a long series of estimation, it is best to take the whites from many incubated eggs, thoroughly mix, and keep in an ice box as stock solution. In this way the albumin seems to keep indefinitely.

² From 5 to 10% excess of acid sometimes gives a clearer solution, but for the purpose of this method, a slight cloud in the albumin is of no consequence as long as it is completely soluble in a little ammonia.

quire much less albumin than the purine bases singly. An ideal protective colloid would be one which would be active with equal efficiency with all the substances. In practical work this inequality does not cause much difficulty, as one uses the smallest amount of colloid necessary for the desired protective action. Under these conditions we have convinced ourselves that precipitation with solutions as weak as 0.0025% is very nearly quantitative. Since the standard is treated in the same way, any deficiency in this direction is eliminated.

Use of Precipitant.—To determine the completeness of precipitation, of each purine by the reagent, nephelometric readings were made, using solutions of different strength, varying from 10.0 to 5.0 mg. per 100 cc. The standard in each case was a 0.01% solution¹ (10 mg. per 100 cc.) of the substance examined, except adenine, which was one-half that strength. The usual care was taken to precipitate the standard and "unknown" under the same conditions. In every instance 10 cc. of the purine solution with 10 cc. of albumin of suitable strength were precipitated with 10 cc. of reagent—prepared according to the preceding directions.

The readings shown in Table II and corresponding curves were obtained.

TABLE II.
Concentrations in mg. per 100 cc.

Substance.	10.0.	9.0.	8.0.	7.0.	6.0.	5.00.	Remarks.
		Readings in millimeters.					
Uric acid 1.....	13.0	14.1	15.7	17.4	19.7	23.1	
Uric acid 2.....	13.0	14.2	15.9	17.7	20.2	23.2	Curve No. 1
Xanthine.....	12.0	12.8	14.2	16.0	18.0	22.0	
Hypoxanthine.....	12.1	12.7	14.3	16.0	18.1	21.0	
Guanine hydrochloride.....	12.1	12.7	14.3	16.3	18.9	21.8	
Mixtures of equal parts of							
Xanthine and hypoxanthine 1..	12.0	12.6	13.9	15.6	18.1	21.1	
Xanthine and hypoxanthine 2..	12.1	12.9	13.8	15.0	16.9	20.1	Curve No. 3
Adenine and guanine 1.....	12.0	12.8	14.3	16.1	19.0	22.9	
Adenine and guanine 2.....	12.1	12.8	14.1	16.0	18.9	22.8	Curve No. 4
Adenine, guanine, xanthine and hypoxanthine 1.....	13.0	13.9	15.3	16.9	18.9	20.7	
Adenine, guanine, xanthine and hypoxanthine 2.....	13.0	14.1	15.6	17.2	19.3	21.7	Curve No. 5
	5.00.	4.50.	4.00.	3.50.	3.00.	2.50.	
Adenine sulfate.....	12.1	13.0	14.6	16.4	19.2	23.1	Curve No. 2

These readings represent the average of readings (usually only 2) of two to three solutions of each concentration. Although all of the curves are below the hypothetical and therefore nearly quantitative, it will be observed that most of the purine curves tend to approach the hypothetical as the ratio of the solutions becomes smaller, while with uric acid and the

¹ In this paper throughout, the weights of substances refer with adenine to the sulfate, and guanine to the hydrochloride; the others to the free bases.

mixture of four purine bases this is not the case. This is best shown by calculating the nephelometric "constant"¹ at different points of the curve.

TABLE III.—NEPHELOMETRIC CONSTANTS.

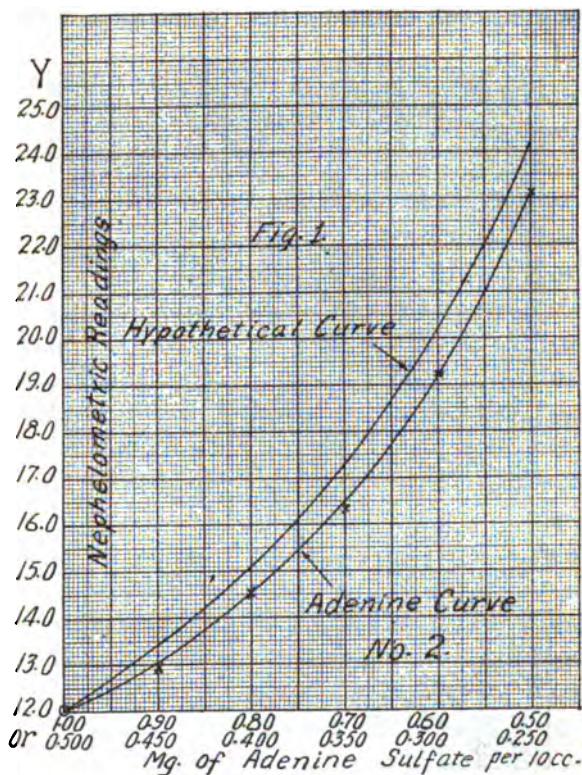
Substance.....	Adenine	Guanine	Xanthine	Hypoxanthine	Purine mixt.	Uric acid
<i>k</i> at ratio of soln. 0.80	0.14	0.22	0.25	0.22	0.16	0.09
<i>k</i> at ratio of soln. 0.50	0.04	0.10	0.09	0.13	0.16	0.11

These facts are undoubtedly due to either the influence of the protective colloid or the solubility of the silver complexes, showing that uric acid precipitation follows the nephelometric curve accurately while the single purine bases show in the weaker solutions a distinct solubility or shift of equilibrium, due to the colloid. This was also demonstrated by adding a large excess of albumin. Thus, the reaction with the purine bases was very much weakened, whereas with uric acid, the reaction was unaffected.

B. Separation of Uric Acid from Purine Bases.

As is well known, on adding Sal-kowski's reagent one obtains uric acid and the other purine bases as silver complexes,

and although there are slight differences in solubility and the speed of reaction between uric acid and the other purine complexes, yet the differences are not enough to serve as a basis for their quantitative separation. The alternative was the elimination of either of these substances from reacting with the reagent. After trying several schemes, the oxidation of uric acid with a suspension of manganese dioxide, seemed very promising. This reagent is used in the Krüger-Schmidt method for a similar purpose. On trying it as recommended by the authors in an acid solution.



¹ Kober, *J. Biol. Chem.*, 13, 491 (1913); also Kober and Egerer, *THIS JOURNAL*, 37, 2373 (1915).

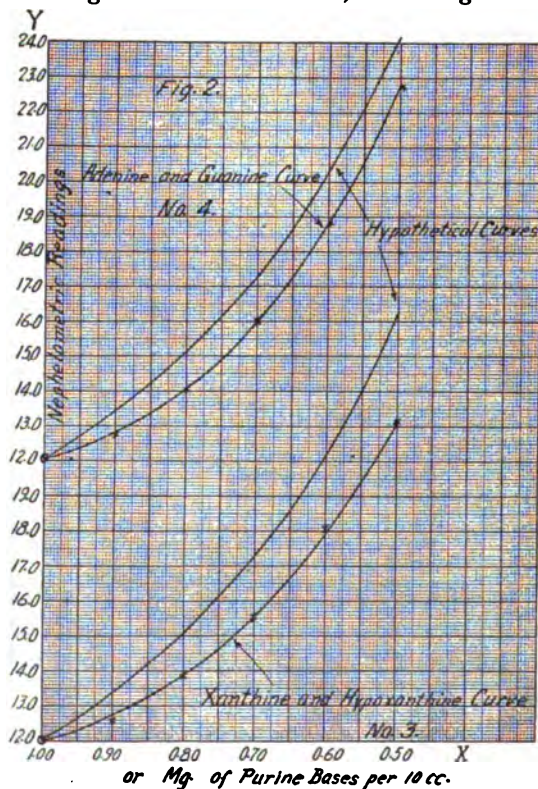
it was found that, even without boiling, not only uric acid was oxidized but some of the other purines as well. On reducing the acidity, the difference between the action on uric acid and other purine bases became sharper, and quantitative.

Oxidizing Reagents.—The details as to the modified reagents and the separation are as follows: 25 g. of potassium permanganate are dissolved in 500 cc. of water, which, on bringing to boiling, are treated with 95% alcohol until all of the permanganate color has disappeared. After filtering and washing with distilled water, the manganese dioxide is suspended in 500

cc. of water. The reagent should give as a fine suspension indefinitely.

The solution containing purine bases and uric acid should be neutralized and to 10 cc. of solution containing about 0.001 g. of the substance

0.1 cc. of 6% ammonium hydroxide (one part of ammonia s. g. 0.90 and three parts water) and 1 cc. of suspension of manganese dioxide are added. After 3 to 4 minutes standing with frequent shaking, the mixture is filtered through paper of good grade until clear and the nephelometric estimation of the purine bases in the filtrate made. The advantage of the reagent is that it



completes the oxidation of uric acid, without introducing any appreciable change in the solution, or leaving any interfering reagents, owing to its insolubility. If the solution to be tested does not contain an electrolyte, it is well to add 1 cc. of a 4% solution of sodium acetate with every cubic centimeter of the reagent, to flocculate the manganese dioxide and thereby increase the efficiency and speed of filtering. Using the reagent as modified, the following results were obtained with the different purines and with uric acid.

Action of Oxidizing Reagent on the Different Purines.—Solutions of the

purines were shaken with the reagent ten minutes, a mixture of the purine bases for thirty minutes, while uric acid oxidation, as Table IV shows, was complete in two minutes. The first column of figures gives the readings of the nephelometer with the solutions after treating with reagent, whereas the second column gives the results without the oxidation mixture, but after making the corresponding dilutions, etc.

TABLE IV.

Substance. Solu. cont. 10 mg. per 100 cc.	Nephelometric readings.		Substance. Solu. cont. 10 mg. per 100 cc.	Nephelometric readings.	
	After shak- ing with manganese dioxide.	Without shak- ing with manganese dioxide.		After shak- ing with manganese dioxide.	Without shak- ing with manganese dioxide.
Xanthine.....	12.0	11.9	Mixtures of equal	12.3	11.9
	12.0	12.0	parts of xanthine	12.1	11.9
Av., 12.0	12.0	12.0	hypoxanthine,	12.1	12.0
			adenine, and	12.1	11.9
Hypoxanthine.....	14.2	14.0	guanine	12.2
	14.0	13.9		12.2
	14.0	14.0			
Av., 14.1	14.0	14.0	Av., 12.2	11.9	
			Uric acid.		
Adenine.....	12.0	12.4	0.5 minute.....	6.6	17.0
	12.4	12.3	1.0 minute.....	5.5	17.0
	12.2	12.0	2.0 minutes.....	3.1	17.0
Av., 12.2	12.2	12.2	5.0 minutes... ..	2.9	17.0
			5.0 minutes.....	3.1	17.0
Guanine.....	10.8	10.8	Reagents and water	3.2	17.0
	11.0	10.6			
	11.0	10.6			
Av., 10.9	10.7	10.7			

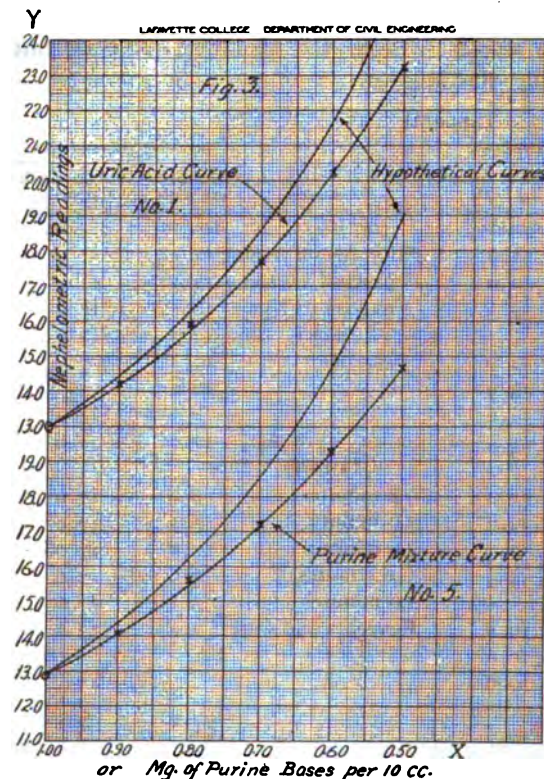
The results show that the amount of purine bases oxidized was inappreciable, except with guanine, which showed a deficiency of about 2%. On treating the mixture of the purine bases for thirty minutes, the total loss was less than 2%, and it is therefore obvious that three minutes' shaking as prescribed will have no appreciable effect on the four purine bases, while the destruction of uric is quantitative.

As the amount of protective colloid necessary for uric acid is much greater than for the other purine bases it was expected that only a slight part of the other purine bases would be precipitated along with the uric acid, and that a control precipitation with the same amount of albumin would be necessary, after the uric acid had been eliminated. On experimentation it was found, however, that when uric acid was present, the other purine bases were thrown down with it quantitatively, notwithstanding the fact that the albumin was about ten times too strong for the purine bases alone.

Therefore, to determine uric acid and the other purine bases separately,

it is necessary (1) to determine the total purine content, using enough albumin to prevent flocculation—that required for an equivalent amount of uric acid, (2) to estimate the purine bases separately, without uric acid, using the smallest

amount of albumin that is necessary to give the desired protective action. The difference between (1) and (2) will give the uric acid content.



At first sight this uncertainty concerning the amount of protective colloid may seem both troublesome and inaccurate, but in reality it is very simple. For definite applications, *i. e.*, for estimating these substances in urine, blood, and ferment work, definite amounts of albumin can be prescribed, for other and new work, albumin of two or three different strengths may be required, but the making of these solutions from a stock solution

(2.0%) and their testing out, will only be a matter of from 15 to 20 minutes.

The correct amount of albumin can be determined very simply by adding three or four different strengths of albumin to the solution containing the uric acid and purine bases, and comparing these, after precipitation, with a standard in the nephelometer. The required strength will be known by the strongest cloud, *i. e.*, the lowest reading. An example will make this clear. When compared to a standard, 5 cc. of a purine mixture (10.0 mg. per 100 cc.) and 10 cc. of reagent gave, with 10 cc. 0.2% albumin, 26.4 mm.; 10 cc. 0.1% albumin, 18.6 mm.; 10 cc. 0.075% albumin, 19.8 mm.; 10 cc. 0.050% albumin, 21.5 mm. In this case 10 cc. of 0.1% of albumin was the necessary amount, while weaker albumin according to the readings allowed some flocculation.

To show that the precipitation is quantitative under these conditions the following results of Table V will suffice:

TABLE V.

Soln. cont. in 100 cc.		Amt. for anal. Cc.	Amt. water added. Cc.	10 cc. albu- min used. %	Read- ing w. 10 cc. reagent. Mm.	Reading of standard.		Ratio of sol.	Total purine bases found in 100 cc. Mg.	Purine bases (net) in 100 cc. Mg.	Uric acid found in 100 cc. Mg.
Purine bases. Mg.	Uric acid. Mg.					1 S. Mm.	1/2 S. Mm.				
00.0	10.0	5.00	0.00	1.0	17.5
10.0	10.0	2.50	2.50	1.0	18.5	17.5	0.938	18.7	9.2	9.5
7.5	10.0	2.50	2.50	1.0	19.7	17.5	0.873	17.5	7.0	10.5
5.0	10.0	2.50	2.50	1.0	16.0	12.4	0.748	15.0	4.9	10.1
2.5	10.0	2.50	2.50	1.0	14.3	17.0	1.21	12.1	2.3	9.8
10.0	7.5	2.50	2.50	0.5	14.5	12.8	0.873	17.5	10.0	7.5
10.0	5.0	2.50	2.50	0.25	17.1	12.8	0.720	14.4	10.0	(4.4)
10.0	2.5	2.50	2.50	0.25	19.2	12.8	0.628	12.6	10.0	2.6
9.2	0.0	5.00	0.10	18.9	17.5	0.916	9.2	9.2
7.0	0.0	5.00	0.05	24.0	17.5	0.696	7.0	7.0
4.6	0.0	5.00	0.05	22.8	12.4	0.485	4.8	4.8
2.3	0.0	5.00	0.05	32.5	17.0	0.463	2.3	2.3
0.0	5.0	5.00	1.0	17.0

These solutions were not treated with manganese dioxide, in order not to introduce any new factors. The first solution given in the table was used as a standard, and the last solution in the table as one-half standard. The results are as accurate as one could expect, when it is considered that an average nephelometric constant of 0.10 was used throughout. Since the albumin varied from day to day and the value for k differs for purines, an appreciable error may have been introduced. As soon as a standard source of albumin is obtained, the percentage accuracy can undoubtedly be considerably increased.

The results of Table VI were obtained by eliminating the uric acid, using the oxidation mixture previously described. Twenty cc. of a mixture of purine bases and uric acid, 2 cc. of sodium acetate and ammonia solution, and 2 cc. of a suspension of manganese dioxide, after shaking 3 to 4 minutes, were filtered and a nephelometric estimation made on the filtrate, as well as on the solution before treatment with oxidation reagents.

TABLE VI.

Soln. cont. in 100 cc.		Reading of soln. Mm.		Reading of standard 0.01 % uric acid. Mm.		Ratio of soln. to standard.		Total purine bases found in 100 cc. Mg.		Purine bases (net) in 100 cc. Mg.		Uric acid found in 100 cc. Mg.	
Purine bases. Mg.	Uric acid. Mg.												
A													
10.0	2.5	14.5	14.7	18.0	18.0	1.26	1.25	12.6	12.5
Filtrate		20.5	21.0	18.0	18.0	0.863	0.838	10.4	10.1	2.2	2.4
B													
10.0	10.0	18.0	19.4	18.0	19.0	1.00	0.952	20.0	19.1
Filtrate		21.0	23.8	18.0	19.0	0.843	0.774	10.1	9.3	9.9	9.8
C													
2.9	10.0	14.5		18.0		1.26		12.6		
Filtrate		23.0		18.0		0.55			3.0		9.6	

In Group *A* the estimation was made by taking for the total purines, 5.00 cc. of the solution, 10 cc. of 0.25% albumin solution, and 10 cc. of reagent; for the filtrates,¹ 5.00 cc. of the solution, 10 cc. of 0.15% albumin and 10 cc. of reagent. In Group *B* the estimation was made by taking for the total purines, 2.50 cc. of solution, 2.50 cc. of water, 10 cc. of 1.0% albumin, and 10 cc. reagent; for the filtrate, 5.00 cc. of solution, 10 cc. 0.15% albumin and 10 cc. of reagent. In Group *C* the estimation was made by taking for the total purines, 2.50 cc. of the solution, 2.50 cc. of water, 10 cc. of 1.0% albumin and 10 cc. of reagent; for the filtrate, 5.00 cc. of the solution, 10 cc. of 0.05% albumin and 10 cc. of reagent, using one-half standard.

III. Directions.

As a standard cloud, uric acid might well be adopted, owing to the purity of the commercial product; and for this purpose we give below the nephelometric value of the different purines (as free bases) in terms of uric acid.

0.100 g. uric acid = 0.031 g. adenine; 0.079 g. guanine; 0.106 g. hypoxanthine; 0.104 g. xanthine; 0.071 g. purine mixture; 0.067 g. adenine and guanine; 0.104 g. xanthine and hypoxanthine.

As it is a safe principle in nephelometry to use as a standard a known amount of the same substance to be determined, the directions for making solutions of each of the purines follow:

One-tenth gram of finely powdered *uric acid* is weighed carefully in a 50 cc. beaker, to which is added 25–30 cc. saturated lithium carbonate (about 1.0%), stirring and powdering with the flat end of a stirring rod until dissolved. The solution is then transferred to a 100 cc. graduated flask with a little water and made up to the mark with 0.2% tricresol.

Xanthine and *hypoxanthine* solutions are made in the same way, except the commercial xanthine which seems to be slightly impure and therefore must be standardized.

¹ As the filtrates were diluted with 4 cc. of water, from the sodium acetate and ammonia and the suspension of manganese dioxide, the ratios of the filtrates was divided in each case by the factor 20/24 or 0.833. Owing to the presence of the salt solution (sodium acetate) it was necessary, as may be observed in the relatively strong filtrates, to increase the strength of albumin from 0.10% to 0.15%.

² S. R. Benedict, *J. Biol. Chem.*, 20, 619–27 (1915), uses a phosphate mixture in connection with acetic acid, which permits the stock solution to be preserved for at least a month. This seems to be an advantage over previous methods of dissolving uric acid.

³ S. S. Graves and P. A. Kober, *THIS JOURNAL*, 36, 751 (1914). As a diluting liquid for organic substances liable to bacterial decomposition, we use an aqueous solution of tricresol (usually 0.2%). This is a much more powerful germicide than chloroform or toluene and causes no trouble in volumetric measurement. Both chloroform and toluene, as is well known, make measuring apparatus unclean and only so that they are unsuitable for accurate work.

For *adenine sulfate* and *guanine hydrochloride*, 25 to 30 cc. of hydrochloric acid (1 vol. of conc. made up to 100 vols. with water) are used instead of lithium carbonate. Warming the solution slightly will hasten solution, but if the substance is sufficiently powdered, this is not necessary.

Directions for making reagents have already been given and in the application of the method to blood and urine, specific details will be given.

General Precautions.—As egg albumin solutions have a tendency to form shreds, it is necessary to avoid their formation or to remove them when formed by careful filtration. The chief cause of their formation seems to be surface tension and therefore any increase of surface through the formation of air bubbles or shaking unnecessarily is to be avoided. In pipeting it is well to allow the solution to drain down the side of the containing vessel or better still to dip the draining pipet into the liquid. Mixing of the solution can be accomplished by gentle rotation. In case filtering is necessary, a long, wide-stem funnel is the most suitable to prevent air bubbles or the formation of drops.

IV. Applications.

A. Urine.—When the reagent is added to urine the complexes of the purines, including uric acid, are formed at once and agglutinate almost immediately (in 1–4 minutes) even when the urine solution is moderately dilute and contains the usual amount of protective colloid. This is doubtless due to the coagulative action of the inorganic salts in the urine. There are two ways to circumvent this difficulty: (1) to offset this action by further dilution and increased amount of albumin, or (2) to remove the interfering salts. This second possibility seems theoretically more desirable. Attempts to throw out calcium as oxalate and magnesium as a carbonate did not produce a solution satisfactory for nephelometric work, probably because other salts are present which cannot be directly precipitated. The final solution of the problem lay, as Folin and Dennis found in their work, in precipitating the purines with the uric acid as complexes and, after centrifuging for a minute or two, pouring off the supernatant liquid containing most of the interfering substances, dissolving the complexes and, after suitably diluting, reprecipitating them. This procedure gives complete control of the precipitating medium and is therefore conducive to accuracy.

Folin and Dennis redissolve uric acid from similar precipitation by means of hydrogen sulfide and hydrochloric acid, boiling off the excess of sulfide. The total elimination of silver at this point is not necessary in our method as our reagent contains silver. Therefore hydrochloric acid alone is sufficient to set free the purine bases which on heating¹ are all redissolved, but some suspended silver chloride remains even after filtering.

¹ Without boiling 98% or more of the purines redissolve, if the solution is not less than 35 cc. for 0.005 g. of purine bases.

In the estimation of total purine bases this silver chloride is of no consequence, but in the estimation of the purines excluding uric acid, the medium for oxidation must be alkaline¹—in which case the silver chloride again forms complexes and in the absence of protective will be filtered off with the oxidation reagent, manganese dioxide. By using a solution of lithium carbonate saturated with hydrogen sulfide, to make the oxidation medium alkaline as given in the general directions, silver chloride is converted into silver sulfide and is completely filtered off with the manganese dioxide. Not only is the silver removed from the sphere of action by this operation, but the uric acid is completely oxidized, and after filtration it will be found that no trace of sulfide remains in the solution, the excess having been removed by the manganese dioxide or changed into some other insoluble substance, as, for example, sulfur.

The removal of alkaline sulfide by a suspension of manganese dioxide seems, as far as we are aware, not to have been used in practice before, and we can strongly recommend it for this purpose. Its advantages over the boiling technic are obvious.

Since the purine reagent is strongly ammoniacal, some inorganic bases of urine, as calcium and magnesium, are thrown down with the purine complexes and find their way into the final solution, but, owing to the presence of protective colloid and their small concentration they do not, as some following experiments show, appreciably affect the estimation of the total purines. In the estimation of purine bases, the alkaline medium necessary for the oxidation of the uric acid also removes these inorganic bases, thus no extra precautions for this purpose are needed.

Technic.—Five cc. of urine are put into a 15 cc. graduated centrifuge tube, 5 cc. of reagent added and the solution centrifuged 1 to 3 minutes—the supernatant liquid is then poured off, 10 cc. of hydrochloric acid (1-100) are added to the residue and the tube placed into boiling water for 2 to 5 minutes. The tube is then cooled and the volume made up to 15 cc. The solution is then centrifuged, or allowed to settle, to remove the larger part of the silver chloride and the liquid drawn off with a pipet—Solution A.

I. Total Purines.—To 3 cc. of Solution A are added, in the order named, 7 cc. of water, 10 cc. of 2% albumin, 0.05 to 0.10 cc. of strong ammonia (s. g. 0.90) to dissolve any silver chloride and 10 cc. of reagent. The suspension is compared in the nephelometer with a standard suspension made by 5 cc. of 0.01% uric acid solution, 5 cc. of water, 10 cc. of 2% albumin and 10 cc. of reagent. This standard is of satisfactory strength for the comparison of most normal urines, but may be made stronger if the urine contains large quantities of purine bases.

II. Purine Bases (excluding Uric Acid).—To 10 cc. of Solution A are

¹ The acid or neutral medium permits oxidation of some of the purines.

added, in the order named, 2 cc. of 1% lithium carbonate solution saturated with H_2S , 2 cc. of lithium carbonate, and 2 cc. of suspended manganese dioxide (see general directions).

This solution, B, allowed to stand for 3 to 5 minutes with occasional shaking, is then filtered until clear.¹ Ten cc. of this solution, B, precipitated by 5 cc. of reagent, are then compared with the standard solution, as described above.

From the fact that the purine bases do not agglutinate in 8 to 10 min. without the addition of albumin, it is assumed that sufficient protective colloid is inherent in the urine to keep them in suspension—since only 5 cc. of 0.2% albumin supply the protection necessary for pure solutions of much greater strength.

III. Uric Acid.—The difference between the total purines and the purine bases is equivalent to the uric acid.

The two determinations are made from 5 cc. of urine, a quantity easily obtainable in normal urinary work. If desirable, however, a smaller quantity will suffice provided the reagents are used in the most concentrated form or the standard solutions made weaker.

Calculations of Results.—The readings of the standard and the unknown solutions are made according to the usual nephelometric directions² and

are then substituted for s and y in the formula $x = \frac{s + sk + \sqrt{(s + sk)^2 - 4sky}}{2y}$

and the value of k being taken as 0.10. The equation is solved for x , the ratio of the solutions, by means of which the amount of substance in grams may readily be calculated.³ The following figures were obtained and are examples of many similar experiments:

TABLE VII (GRAMS PER LITER).

Urine.	Total purines.	Purine bases.	Nephelometric method. Uric acid (by dif.).	Method of Folin and Dennis. Uric acid.
Normal I (human).....	0.745	0.089	0.656	0.584
Normal I (human).....	0.720	0.086	0.634	0.595
Normal I (human).....	0.720	0.083	0.637	0.560
Normal I (human).....	0.745	0.086	0.659	0.562
Normal I (human).....	0.730	0.085	0.645
Av.,	0.730	0.086	0.646	0.578

These results show that in our hands the Folin and Dennis colorimetric method gave from 8 to 10% lower values for uric acid than the nephelometric. We are not ready to decide which of these two methods is nearer

¹ Usually two filtrations are sufficient owing to the presence of salts in the urine but in pure solutions it is well to add some electrolyte, *e. g.*, 1 cc. of 4% solution of sodium acetate.

² Kober, *J. Biol. Chem.*, 13, 491 (1913).

³ The slide rule is a great time saver in these calculations.

the truth, but the following points have been observed: (1) that in pure solutions both methods seem equally accurate; (2) in practical urinary work, as indicated above, the nephelometric method may give results which are slightly too high, owing to the presence of some insoluble salts, but the error, as experiments below show, cannot be more than 2% and is probably very much smaller. The Folin and Dennis colorimetric method, however, in our hands and others, shows the possibility that it gives results which are too low. As Folin and Dennis have observed, their color fades on standing, but contrary to their statement, the color produced by the urine unknown, fades very much more rapidly than the color of the standard. In work done so far on urines with the colorimetric method it has been hard to get two readings which agree, the second reading always being higher than the first; thus, for example, a uric acid estimation in urine made according to their directions gave on the first reading 12.0 mm., on the second reading made as soon as possible after the first, 12.4; two minutes after the second reading, a third estimation gave 14.2 and the 4th reading made after the lapse of another five minutes, gave 17 mm.; thus in about ten minutes almost 50% of the color, as compared to the standard had faded. We are not sure that our technic was faultless but the estimations were made following the directions as closely as possible. If this fading,¹ which has been noted by others, follows the law of mass action, and it probably does, the fading during the first minute or two must be very appreciable and may account for the difference between the colorimetric and nephelometric methods.

Experiments to Show the Effect of Salts in Urine on the Total Purine Estimation.—I. Urine solutions, prepared according to the preceding directions, show none or a very slight cloud when treated with 2% albumin and reagent made without silver (other constituents being the same) in amounts prescribed for the estimation of total purines. It is to be remembered that the ammonia in the reagent is more than ample to dissolve any insoluble compound of silver with a urinary substance, such as phosphate, chloride, etc., except purine complexes.

II. Urine solutions, prepared according to the preceding directions, upon *oxidation in acid medium* which destroys uric acid and most of the purines after the addition of albumin and normal reagents, showed only a trace of cloud as compared with a standard containing only albumin and reagent.

III. To the filtrates from oxidized urine solutions (see II) were added known amounts of uric acid (0.0005 g.) which were recovered with a slight increase (less than 2%).

¹ S. R. Benedict, *J. Biol. Chem.*, 20, 619-27 (1915), obtains about 18% more color using KCN as a solvent for the silver complex. Benedict thinks this is due to the marked diminution in the rate of fading of the color. As the fading has not been entirely eliminated, one would expect the results to be still somewhat too low.

Readings found.....	15.9	15.7	15.8	16.2
Readings expected.....	16.2	16.2	16.2	16.2

These experiments show that in urinary medium, from which all of the uric acid and most of the purine bases had been oxidized and to which a known amount of uric acid had been added, we were able to obtain very nearly quantitative figures. Making no allowance for traces of unoxidized purines, the error is about 2%, but we are not certain that the acid medium permitted the oxidation of all of the purines, and if allowance is made for this factor, then the error in our nephelometric method is very much smaller.

B. Blood.—In the estimation of purine bases, as with most constituents of the blood, it is necessary to remove the bulk of the proteins. For the quantitative precipitation of the coagulable proteins 5 volumes of 3% sulfosalicylic acid¹ have proved very satisfactory—but, owing to the development of the yellow color² in the sulfosalicylic acid filtrate, when made alkaline, by the ammonia of the purine reagent, the direct estimation of the purines in the blood filtrates with this protein precipitant was found nephelometrically unsuitable.

Greenwald's³ discovery of trichloroacetic acid as a reagent for the removal of blood proteins, is of great service for the estimation of purines in blood. It gives filtrates which are clear and free from proteins, and enables us to estimate the purine bases in them directly, after centrifuging off the calcium as oxalate.

Our intention was to apply our reagent to the estimation of purines in different kinds of blood, normal and pathological, but two obstacles have prevented us. (1) For some time we lacked a suitable nephelometer⁴—one which held at least 100 mm. of liquid. (2) After getting such an instrument we now lack the opportunity to finish the work on blood. We are therefore compelled to content ourselves with an outline of our blood procedure and a few qualitative experiments.

As sheep blood contains no appreciable amount of free purine bases, it is well adapted for experimental work in developing this method. There-

¹ Kober, *THIS JOURNAL*, 35, 290, 1585 (1913).

² Probably a nitrate reaction.

³ *J. Biol. Chem.*, trichloroacetic acid, while very efficient as a precipitant for strong solutions of protein, is, however, not so suitable for nephelometric estimation of proteins.

⁴ As the amount of purine bases in some kinds of blood is extremely small, it was necessary to have about 100 mm. of liquid under observation. The instruments used by us heretofore allowed not more than 40 mm. of liquid. We were, therefore, compelled to design an instrument of larger capacity, and because of the difficulty of getting suitable optical glass, owing to the European war, the whole problem was delayed.

The new instrument, having many improvements over the Duboscq, such as a Lummer-Brodhun eyepiece, adjustable vernier, black glass plungers and other new devices, will be described in a separate paper, and can be obtained from Lenz and Naumann, 17 Madison Ave., New York City, for about 1/3 the original price, \$36.00.

fore, the quantitative recovery of known amounts of purine bases added to the blood, will suffice to show the applicability of the method.

The following (Table VIII) qualitative preliminary experiments with the method were made with sheep blood, April 27, 1915:

TABLE VIII.

No.	Blood taken. Cc.	Purine bases added (mixture). Mg.	Trichloroacetic acid added for removal of protein. Cc. of 5%.	Filtrate taken for test. Cc.	Precipitate found (Cloud).
(1)	20.0	0.25	100	80	+ + +
(2)	20.0	0.25	100	80	+ + +
(3)	20.0	0.25	100	80	+ + +
(4)	20.0	0.25	100	80	+ + +
(5)	20.0	100	80
(6)	20.0	100	80
(7)	H ₂ O	0.25	100 H ₂ O	80	+ + +

These experiments showed that the conditions for the direct nephelometric estimation of uric acid and other purine bases in blood, after the removal of the blood protein with Greenwald's reagent and of calcium with ammonium oxalate, to be very favorable.

V. Summary.

I. Salkowski's reagent for purine bases has been modified to meet nephelometric conditions, and it is shown that the reagent will precipitate xanthine, hypoxanthine, guanine, adenine and uric acid quantitatively in very dilute solutions (0.0002%).

II. The use of a protective colloid has been introduced—clear solutions of egg albumin—for the purpose of keeping the precipitates in suspension so that they may be estimated nephelometrically.

III. It has been shown that the suspension of manganese dioxide *is an alkaline, instead of in an acid medium*, as has been used heretofore, will oxidize uric acid completely in 1 to 3 minutes, and leave the other purines practically unattacked.

IV. It has been shown that manganese dioxide is an excellent reagent for the removal of alkaline sulfides from solution without the usual boiling technic, and without introducing any interfering reagents in the solution.

V. It has been shown that uric acid, and other purine bases in urine, may be quickly and fairly accurately estimated with the nephelometer.

VI. It has been shown that 5 volumes of 3% sulfosalicylic acid is an excellent reagent for removing all coagulable protein from blood. By

¹ In each case, to 80 cc. of clear filtrate were added 5 cc. of oxalic acid (saturated) solution and 5 cc. of strong ammonia (s. g. 0.90). After centrifuging off the precipitate of oxalates, and taking an aliquot portion (80 cc.), 5 cc. of a strong solution of ammoniacal silver nitrate were added (26.0 g. silver nitrate, 50 cc. of water, 66.0 cc. of ammonia (s. g. 0.90). This reagent contains no chlorides, as blood chlorides are sufficient to prevent the reduction of silver.

centrifuging 1 to 2 minutes after the precipitation with sulfosalicylic acid, the great bulk of protein can be removed, and if the supernatant liquid is shaken with a little talcum to cause agglutination of any remaining suspended protein, a perfectly clear filtrate can be obtained in 5 to 10 minutes without boiling.

VII. It has been shown that 5 volumes of Greenwald's reagent (5%) for the removal of blood protein is equally efficient, and that it has the advantage that it forms with ammonia no yellow color.

VIII. An outline of the technic for the estimation of purine bases in blood is given.

NEW BOOKS.

Surface Tension and Surface Energy and their Influence on Chemical Phenomena.

By R. S. WILLOWS AND E. HARSCHER. Pp. viii + 80; 17 illustrations. P. Blakiston's Son & Co., 1915. Price, \$1.00 net.

This book, which is based upon a course of lectures delivered as a continuation of another set on colloidal chemistry, has for its object the consideration of the theory of those surface interactions which are evidenced experimentally by the phenomenon of adsorption. In the main, the treatment is excellent, and the book will be found an especially valuable résumé of the subject by those who are interested in the chemistry of colloids, whether from the biological or from the purely chemical side.

Unfortunately, by an oversight, it is made to appear on page 5 that the surface tension, itself of a liquid, is related to its critical temperature in the same way as Ramsay and Shields have found the more complicated function—surface tension times the two-thirds power of molecular weight over density—to be. This was proven long since to be incorrect, and in fact was the reason why the classical work of Ramsay and Shields was undertaken.

J. L. R. MORGAN.

The Electrical Nature of Matter and Radioactivity. By HARRY C. JONES. Pp. viii

+ 212. Third Edition. Completely Revised. New York: D. Van Nostrand Company, 1915. Price, \$2.00 net.

The viewpoint of this book is essentially that of about 1905, despite the two revisions which the work has undergone. The important work of Fajans on the electrochemical properties of the radioelements, and Soddy's rules for the effect of alpha and beta ray changes on the valence of the radioelements, have thrown much light upon the chemical nature of these elements, have made it possible to fit them into the periodic table and have given us a new notion in regard to certain elements—isotopes, as Soddy has called them. For example, thorium and ionium are isotopes, as are also radium B, radium D, radium G, and lead. These elements, of different atomic weight, are chemically and spectroscopically

identical. This work which, with the resulting hypotheses, has brought order to our understanding of the chemical properties of the radioelements, is second only in importance to the disintegration hypothesis of Rutherford and Soddy, which brought an explanation for the production and decay of radioactive substances. Soddy's and Fajan's work is not even mentioned in the last edition of Prof. Jones' book. The important work of Moseley, and Rutherford and Andrade on X-rays and gamma rays is not mentioned, and treatment of the more recent views as to the nature of the atom is limited to two paragraphs of eleven lines.

Data are still quoted which are now known to be incorrect (heat produced by radium, pp. 110 and 117; and the volume of a curie of emanation). Many pages are devoted to the discussion of subjects about which there is now not the uncertainty that prevailed in 1905. For example, the general reader may find it somewhat confusing to read several pages of argument and hypothetical reasoning which prove that Runge and Precht's calculated value for the atomic weight of radium, 257.8 (which is based on the spectrum lines of radium and certain relations between the series spectrum lines of elements and their atomic weight) is correct, while the directly determined value, of about 225, is incorrect, and then find in the last six lines at the end of the chapter, the results obtained by Mme. Curie, Thorpe, Gray and Ramsay, and Hoenigschmidt, all of which go to show that the lower atomic weight is correct. Errors have crept through uncorrected, as for example p. 96 (cf. also p. 115), where it is stated that "the alpha particle has a mass of the order of magnitude of about twice that of the hydrogen ion," and (pp. 73-96) the general statement that all of the radioactive substances give off alpha rays. This last statement is later qualified when specific radioelements are discussed.

The reviewer found many points to which exception could be taken. While the book contains much interesting matter for the general reader, there is much which is now superfluous, and the inadequate revision has been such as to lead to the possibility of confusion to the reader. It is no simple task to revise such a work so as to bring it down to date, and the method which has been adopted in this book of adding a few lines at the end of the chapter is exceedingly poor. It is the reviewer's opinion that this work as presented in the first edition is far better than in this so-called revised edition, since in a "revised edition" one would infer that the work had been revised, and this is decidedly not the case.

C. H. VIOL.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON
ATOMIC WEIGHTS, 1916.

Received September 13, 1915.

Although many scientific activities have been interrupted by the European war, a fair number of atomic-weight determinations have appeared since the report for 1915 was prepared. They are, briefly, as follows:

Carbon.—Richards and Hoover¹ neutralized sodium carbonate with hydrobromic acid which had been standardized against silver. In this way the ratio of carbonate to silver was determined. With $\text{Ag} = 107.88$, $\text{Br} = 79.916$ and $\text{Na} = 22.995$, $\text{C} = 12.005$.

Sulfur.—Atomic weight also determined by Richards and Hoover,² who measured the ratio between sodium carbonate and sulfate. With the values previously assigned to sodium and carbon, $\text{S} = 32.060$.

Iodine.—By the direct analysis of iodine pentoxide, Guichard³ finds $\text{I} = 126.92$.

Copper.—The electrolytic ratio between copper and silver has been remeasured by Shrimpton,⁴ with $\text{Ag} = 107.88$, $\text{Cu} = 63.563$, as the mean of ten determinations.

¹ THIS JOURNAL, 37, 95.

² *Ibid.*, 37, 108.

³ *Compt. rend.*, 159, 185.

⁴ *Proc. Phys. Soc. London*, 26, 292.

Nickel.—Oechsner de Coninck and Gerard,¹ by reduction of nickel oxalate in hydrogen, find $Ni = 58.57$. Few details are given.

Cadmium.—By the electrolysis of cadmium chloride Baxter and Hartmann² find $Cd = 112.417$. This confirms the earlier work of Baxter and his colleagues, and gives cadmium a much higher value than was found by Hulett.

Mercury.—By the synthesis of mercuric bromide Baker and Watson³ find $Hg = 200.57$, when $Br = 79.92$. This value is near that found by Easley.

Lead.—By the analysis of lead bromide Baxter and Thorvaldsen⁴ find $Pb = 207.19$. With the chloride, Baxter and Grover⁵ obtained the value 207.21, and with the bromide, 207.19. These determinations were made with *normal* lead from widely separated and dissimilar sources, and are highly concordant.

The value $Pb = 207.20$ will be adopted in the table of atomic weights.

Lead from radioactive minerals, however, has been found to differ in atomic weight from ordinary lead. For lead from thorite Soddy and Hyman⁶ found atomic weights ranging from 208.3 to 208.5. Maurice Curie⁷ studied lead from pitchblende, carnotite, and yttrantalite, and obtained values from 206.36 to 206.64. Lead from monazite and galena was more nearly normal. Hönigschmid and Horowitz⁸ studied lead from pitchblende, and by analyses of the chloride found $Pb = 206.735$. Richards and Lembert⁹ made six series of analyses of lead chloride prepared with lead derived from carnotite, thorianite, pitchblende and uraninite, the mean values being $Pb = 206.59, 206.81, 206.83, 206.57, 206.86,$ and 206.36. These figures, although each series is concordant within itself, show that radio lead is variable in its atomic weight, and that the single, definite metal is yet to be completely isolated. Indeed, the relations between radio lead (or leads) and ordinary lead are still obscure.

Tin.—Briscoe,¹⁰ by analyses of the tetrachloride $SnCl_4$ finds $Sn = 118.70$, when $Ag = 107.88$ and $Cl = 35.457$. This new value, which was determined with all modern precautions, will be adopted in the table.

Tantalum.—Sears and Balke,¹¹ in a preliminary series of determinations

¹ *Compt. rend.*, **158**, 1345.

² *THIS JOURNAL*, **37**, 113.

³ *J. Chem. Soc.*, **107**, 63.

⁴ *THIS JOURNAL*, **37**, 1021.

⁵ *Ibid.*, **37**, 1027.

⁶ *J. Chem. Soc.*, **105**, 1402.

⁷ *Compt. rend.*, **158**, 1676.

⁸ *Z. Electrochem.*, **20**, 457.

⁹ *THIS JOURNAL*, **36**, 1329.

¹⁰ *J. Chem. Soc.*, **107**, 63.

¹¹ *THIS JOURNAL*, **37**, 839.

of the ratio between TaCl_5 and Ag, obtained values for Ta ranging between 180.90 and 182.14. The research is to be continued.

Praseodymium.—Baxter and Stewart,¹ in a long series of concordant analyses of the chloride PrCl_3 , find $\text{Pr} = 140.92$. The rounded-off figure 140.9 will be adopted here.

INTERNATIONAL ATOMIC WEIGHTS, 1916.

Symbol.	Atomic weight.	Symbol.	Atomic weight.
Aluminum.....Al	27.1	Molybdenum.....Mo	96.0
Antimony.....Sb	120.2	Neodymium.....Nd	144.3
Argon.....A	39.88	Neon.....Ne	20.2
Arsenic.....As	74.96	Nickel.....Ni	58.68
Barium.....Ba	137.37	Niton (radium emanation)....Nt	222.4
Bismuth.....Bi	208.0	Nitrogen.....N	14.01
Boron.....B	11.0	Osmium.....Os	190.9
Bromine.....Br	79.92	Oxygen.....O	16.00
Cadmium.....Cd	112.40	Palladium.....Pd	106.7
Caesium.....Cs	132.81	Phosphorus.....P	31.04
Calcium.....Ca	40.07	Platinum.....Pt	195.2
Carbon.....C	12.005	Potassium.....K	39.10
Cerium.....Ce	140.25	Praseodymium.....Pr	140.9
Chlorine.....Cl	35.46	Radium.....Ra	226.0
Chromium.....Cr	52.0	Rhodium.....Rh	102.9
Cobalt.....Co	58.97	Rubidium.....Rb	85.45
Columbium.....Cb	93.5	Ruthenium.....Ru	101.7
Copper.....Cu	63.57	Samarium.....Sa	150.4
Dysprosium.....Dy	162.5	Scandium.....Sc	44.1
Erbium.....Er	167.7	Selenium.....Se	79.2
Europium.....Eu	152.0	Silicon.....Si	28.3
Fluorine.....F	19.0	Silver.....Ag	107.88
Gadolinium.....Gd	157.3	Sodium.....Na	23.00
Gallium.....Ga	69.9	Strontium.....Sr	87.63
Germanium.....Ge	72.5	Sulfur.....S	32.06
Glucinum.....Gl	9.1	Tantalum.....Ta	181.5
Gold.....Au	197.2	Tellurium.....Te	127.5
Helium.....He	4.00	Terbium.....Tb	159.2
Holmium.....Ho	163.5	Thallium.....Tl	204.0
Hydrogen.....H	1.008	Thorium.....Th	232.4
Indium.....In	114.8	Thulium.....Tm	168.5
Iodine.....I	126.92	Tin.....Sn	118.7
Iridium.....Ir	193.1	Titanium.....Ti	48.1
Iron.....Fe	55.84	Tungsten.....W	184.0
Krypton.....Kr	82.92	Uranium.....U	238.2
Lanthanum.....La	139.0	Vanadium.....V	51.0
Lead.....Pb	207.20	Xenon.....Xe	130.2
Lithium.....Li	6.94	Ytterbium (Neoytterbium)....Yb	173.5
Lutecium.....Lu	175.0	Yttrium.....Yt	88.7
Magnesium.....Mg	24.32	Zinc.....Zn	65.37
Manganese.....Mn	54.93	Zirconium.....Zr	90.6
Mercury.....Hg	200.6		

¹ THIS JOURNAL, 37, 516.

Ytterbium.—Blumenfeld and Urbain,¹ in a series of analyses of the sulfate $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, find $\text{Yb} = 173.54$. This may be rounded off to 173.5.

Uranium.—Hönigschmid,² from analyses of the bromide UBr_6 , finds $\text{U} = 238.18$. The value 238.2 may properly be adopted.

At the meeting of the International Congress of Applied Chemistry, in 1912, a resolution was passed favoring delay in changes in the table of atomic weights. In accordance with the desire so expressed, no changes have since been made, but several now seem to be necessary. These relate to C, S, He, Sn, Pb, Ra, U, Yt, Pr, Yb, Lu, and U. The reasons for the changes, which are small, may be found in this and the three preceding reports. They are based upon new determinations, which seem to be better than the old.

(Signed)

F. W. CLARKE,
T. E. THORPE,
W. OSTWALD.

NOTE.—Professor Urbain, because of an official connection with the military service of France, is debarred from signing any international report during the war. Otherwise he would approve this report.

F. W. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR PRESSURE OF THALLIUM AMALGAMS.

By JOEL H. HILDEBRAND AND ERMON DWIGHT EASTMAN.

Received September 3, 1915.

The work presented in this paper is in continuation of the series of investigations undertaken by one of us on the laws of concentrated solutions. The previous papers include vapor pressure measurements of zinc,³ silver,⁴ gold,⁴ and bismuth⁴ amalgams, and also a discussion of e. m. f. measurements to be found in the literature on the amalgams of zinc, tin, lead, thallium, indium and cadmium.¹ We would refer to the earlier papers for the progress of the work up to this point, as well as for references to the literature.

The experimental procedure was essentially the same as that used in working with bismuth amalgams, so that it is unnecessary to repeat its description here. The thallium used was analyzed for lead, two experiments giving 0.3% and 0.25%, respectively, an amount of impurity far too small to have any effect on these measurements.

¹ *Compt. rend.*, 159, 325.

² *Z. Electrochem.*, 20, 452.

³ J. H. Hildebrand, *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 22, 139, 147; *Trans. Am. Electrochem. Soc.*, 22, 319, 335 (1912); *THIS JOURNAL*, 35, 501 (1913).

⁴ Ermon D. Eastman and J. H. Hildebrand, *THIS JOURNAL*, 36, 2020 (1914).

The results of the measurements are summarized in Table I. Under n in the third column, are given values of the number of mols of mercury per mol of thallium. (In previous papers this ratio was denoted by N . The desirability of using the large letter for the mol-fraction, here $n/(n+1)$ has suggested the present change.) The letters p and p_0 denote the vapor pressure of mercury over the amalgam and over pure mercury, respectively. Instead of giving the individual readings of the pressures, a number of which were made at each concentration, we report the number of these observations and the "probable error" of the mean values given in the table calculated by the usual formula.

Thallium amalgams are especially interesting because of the existence of one, and, so far as is known, only one compound in the solid state. The freezing-point measurements of Kurnakow¹ show very clearly the separation of a solid compound of the composition TiHg_2 . We may conclude, furthermore, from the absence of a peak to the melting point curve for this compound, that it is considerably dissociated in the liquid amalgam. The addition of either mercury or thallium to the liquid having a composition corresponding to TiHg_2 fails to lower its freezing point very much, indicating that the substance added is already present to a large extent in the liquid, and hence a further addition does not produce the increase in concentration that would be produced if the compound were but slightly dissociated. The existence of TiHg_2 in dilute liquid amalgams has been further concluded by G. McP. Smith² on the basis of the rate of diffusion of thallium in mercury. However, the application of Raoult's law to the e. m. f. of dilute amalgams has been shown by one of us³ to indicate the existence of TiHg_2 , breaking down in some way as the amalgams become more concentrated.

TABLE I.

Wt. Tl.	Wt. Hg.	n .	$n/n+1$.	No. of obs.	Temp.	p/p_0 obs.	Prob. error.	p/p_0 calc.
1.673	36.408	22.1	0.957	6	329.0	0.955	0.0003	0.952
1.163	18.70	16.35	0.942	5	327.4	0.938	0.0004	0.935
1.673	17.68	10.74	0.915	5	328.3	0.901	0.0004	0.901
1.163	9.554	8.35	0.893	5	327.5	0.875	0.0004	0.874
3.207	16.10	5.12	0.836	5	322.9	0.803	0.0003	0.803
3.207	9.069	2.87	0.742	5	327.5	0.690	0.0003	0.691
4.162	8.097	1.978	0.664	5	326.1	0.602	0.0004	0.603
3.207	5.029	1.590	0.614	5	327.6	0.548	0.0005	0.550
7.390	7.196	0.990	0.497	6	325.2	0.433	0.0006	0.433
7.720	4.033	0.531	0.347	10	327.1	0.293	0.0011	0.293
7.221	1.796	0.253	0.202	8	324.0	0.166	0.0016	0.166

It will be seen from the measurements in Table I, and from their graphic

¹ *Z. anorg. Chem.*, 30, 86 (1902).

² *THIS JOURNAL*, 36, 847 (1914).

³ *Loc. cit.*

representation in Fig. 1, that the relative vapor pressures of the amalgams, p/p_0 , are always less than the apparent mol-fraction of mercury in the amalgam, instead of equal to it, if Raoult's law held in its simplest form. The deviation is in the direction that we should expect if a compound were formed reducing the mol-fraction of free mercury. If the formation of TlHg_2 in the liquid were complete, then there would be $n - 2$ mols of free mercury and Raoult's law would give $p/p_0 = (n - 2)/(n - 1)$. This equation makes p/p_0 much less than is found by experi-

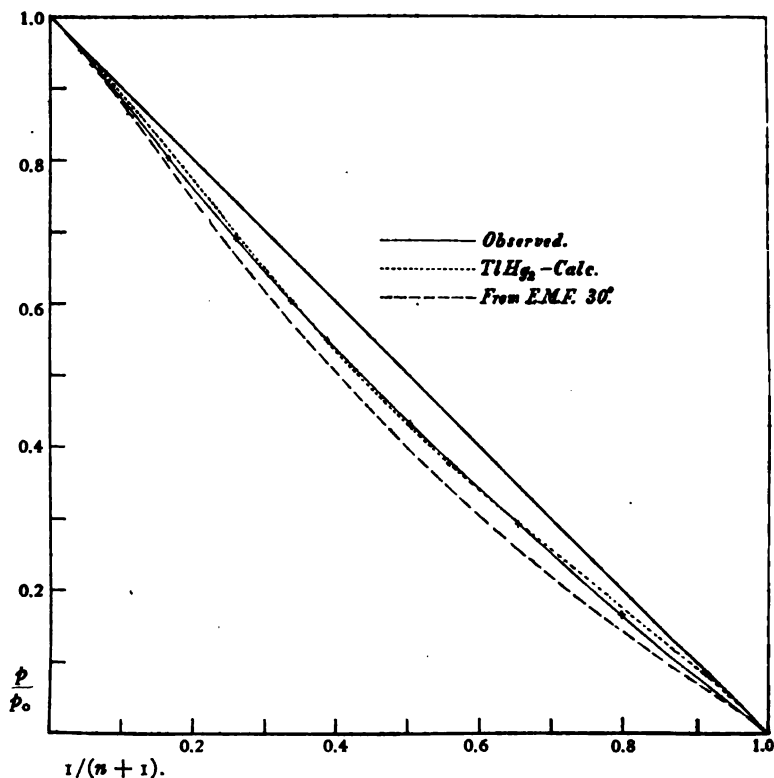


Fig. 1.

ment, so that we next assumed that this same compound is formed partially. Representing by z the number of mols of TlHg_2 formed from 1 mol of thallium and n mols of mercury, we would have present in the solution $1 - z$ mols of thallium and $n - 2z$ mols of mercury, the total number of mols being $n - 2z + 1$. Since the three substances are in equilibrium according to the equation $\text{Hg} + 2\text{Tl} = \text{TlHg}_2$, we can apply the mass-law, using mol fractions for concentrations, obtaining the equation

$$(1 - z)(n - 2z)^2 = Kz(n - 2z + 1)^2 \quad (1)$$

By Raoult's law in its corrected form we have

$$\frac{p}{p_0} = \frac{n - 2z}{n - 2z + 1}. \quad (2)$$

From these two equations it is possible to eliminate z , giving p/p_0 in terms of K and n . It is mathematically simpler, however, to assign values to z and solve separate simultaneous equations for p/p_0 and n . For this purpose we can combine the above equations, obtaining

$$\frac{p}{p_0} = \frac{Kz}{1 - z},$$

and to get n we can transpose Equation 2, getting

$$n = 2z + \frac{1}{(p_0/p) - 1}.$$

In Fig. 1 the dotted curve gives the resulting values putting $K = 1.3$. It is obvious that there is an approximate, but by no means perfect, agreement with the experimental values. The actual pressures are less than given by the equation, probably at the concentrated, and certainly at the dilute, end of the curve. A change in the value assumed for K would not help matters. Making the curve fit at the ends would throw it off at the middle.

It is not unreasonable, however, that there should be this deviation from the simple assumption of $TlHg_2$. The well-known analogy between thallium and the alkali metals makes it natural to consider the possibility of compounds containing more mercury than $TlHg_2$, for in addition to the very stable $NaHg_2$ and KHg_2 , there exist solid compounds containing several more atoms of mercury per atom of alkali metal. It is not unlikely, therefore, that some higher thallium-mercury compound exists in the liquid amalgam, and it may be added that the freezing-point measurements of Kurnakow are not numerous enough to exclude even the possibility of its existence in the solid form. The existence of, say, $TlHg_3$, would explain the deviation from the calculated curve in the dilute amalgams.

A quite different explanation would be that Raoult's law, even when modified to account for chemical reactions in the solution, is not able to express the vapor pressure accurately. This kind of deviation has been discussed in connection with bismuth amalgams, also in a paper by one of us on the entropy of vaporization,¹ and will be again referred to later.

It is very important to compare the results of the above vapor pressure measurements with the measurements of the e. m. f. between thallium amalgams of different concentration, published by Richards and Wilson,² and Richards and Daniels.³ The evidence as to the constitution

¹ Joel H. Hildebrand, *THIS JOURNAL*, 37, 970 (1915).

² *Pub. Carnegie Inst. Wash.*, 118; *Z. physik. Chem.*, 72, 129 (1910).

³ *Trans. Am. Electrochem. Soc.*, 22, 343 (1912).

of thallium amalgams afforded by the former measurements has been already presented by one of us¹ by a method which may be outlined briefly as follows:

If one mol of thallium combines with m mols of mercury in an amalgam containing, altogether, one mol of thallium and n mols of mercury, there would be present $n - m$ mols of free mercury and one mol of compound, or a total of $n - m + 1$ mols. Applying Raoult's law to the we get

$$\frac{p}{p_0} = \frac{n - m}{n - m + 1}. \quad (3)$$

Now, it has been shown in the first papers on amalgams that the following exact equation applies to the e. m. f. of concentration cells of this type

$$\nu EF = RT \int n d \ln p \quad (4)$$

Here ν denotes the valence of the metal dissolved in the mercury. The other letters have their usual significance in this connection. Integrating this with the aid of the preceding relation between n and p we obtain the expression

$$\nu EF = RT m \ln \frac{n_2 - m}{n_1 - m} - RT(m - 1) \ln \frac{n_2 - m + 1}{n_1 - m + 1}. \quad (5)$$

This formula has been applied to the measurements of Richards and Wilson in the earlier papers, and has been shown to give very good agreement when m is 5 or 6, indicating the presence of TlHg_5 or TlHg_6 in the most dilute amalgams. Since then, however, the single measurement reported by Richards and Daniels has been considered. They find, at 30° , e. m. f. of 76.3 mv. between a pair of amalgams containing 3.73% and 21.722% of thallium, respectively. Calculated by the equation for an ideal solution,

$$\nu EF = RT \ln \frac{n_2 + 1}{n_1 + 1},$$

this should be 46.0 mv., and calculated for TlHg_2 , by putting $m = 2$ in Equation 5, we get 81.0 mv. We could conclude from this evidence that in the most concentrated amalgams even TlHg_2 is somewhat dissociated.

Where several partly dissociated solvates exist together in solution the application of Raoult's law to the integration of Equation 4 becomes exceedingly complicated, and with no external evidence for the form of any of these solvates except TlHg_2 , any such calculation would be worth the time and labor it would involve.

It is possible, however, to make a further and exact comparison between vapor pressure and e. m. f. data, and we shall find that the de-

¹ Hildebrand, *THIS JOURNAL*, 35, 501 (1913).

tion from Raoult's law is of the same type in both cases, the difference being due only to the difference in temperature at which the two sets of measurements were carried out.

In the discussion of the results with bismuth amalgams we have shown that the equation of Van Laar¹ for the vapor pressure of liquid mixtures can be used very satisfactorily as an empirical equation, probably to fit any type of vapor pressure curve. We will write it as follows:

$$\frac{p}{p_0} = \frac{n}{n+1} e^{\frac{b}{(1+cn)^2}} = \frac{n}{n+1} 10^{\frac{a}{(1+cn)^2}} \quad (6)$$

where a , b , and c are constants and e the base of natural logarithms. It was found that the observed vapor pressures were given very closely indeed on putting $a = -0.0960$ and $c = 0.263$ in this equation. The values shown in the last column of Table I were thus obtained and may be regarded as the "smoothed out" observations given in the seventh column of the same table. The close agreement attests the accuracy of the experimental work. If this form of vapor pressure equation is used to integrate the fundamental e. m. f., Equation 4, one obtains the following equation:

$$e_{EF} = RT \ln \frac{n_2 + 1}{n_1 + 1} + 0.4343 \frac{a}{c} RT \left[\frac{1 + 2cn_2}{(1 + cn_2)^2} - \frac{1 + 2cn_1}{(1 + cn_1)^2} \right] \quad (7)$$

This equation is found to fit the results of Richards and his co-workers very accurately when we take $a = -0.1791$ and $c = 0.345$, the simplified expression being then, for 30° ,

$$E = 0.06012 \log \frac{n_2 + 1}{n_1 + 1} + 0.06069 \left[\frac{1 + 0.69n_1}{(1 + 0.345n_1)^2} - \frac{1 + 0.69n_2}{(1 + 0.345n_2)^2} \right]$$

The first term of the right-hand member of this equation represents the e. m. f. of the ideal solution, obeying Raoult's law in its simplest form.

TABLE II.

% Tl.	n .	E (mv. at 30°).	
		Observ.	Calc.
0.1575	644.6	10.09	10.39
0.2294	442.3	22.61	22.61
0.5249	192.7	37.13	37.07
1.846	54.08
3.736	26.204	76.31	76.32
21.722	3.6649		

The figures in Table II give the results in millivolts between each pair of concentrations.² It will be seen that the agreement between the calculated and observed values is excellent throughout the entire range of

¹ *Z. physik. Chem.*, **72**, 723 (1910); **82**, 599 (1913).

² A slight error made throughout in the values for n in the earlier papers has been here corrected, which accounts for the slight differences. The influence on the values for e. m. f. is negligible.

concentration represented by the data. The graphic comparison is perhaps more striking, as given in Fig. 2. The four curves give the deviation of the e. m. f. from Raoult's law according to the assumption of com-

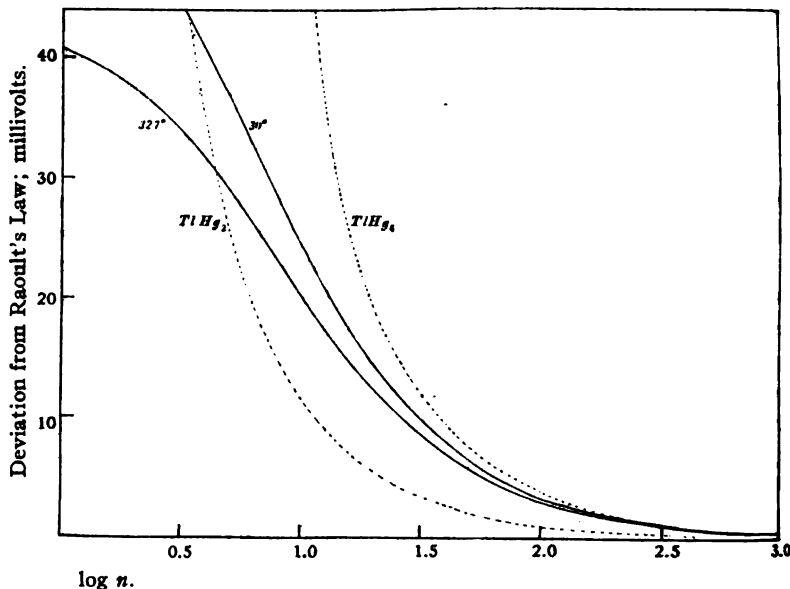


Fig. 2.

plete formation, first, of TIHg_4 , second, of TIHg_2 , third, according to the actual measurements from the Harvard laboratory at 30° , and fourth, calculated from the values of a and c which fit the vapor-pressure measurements at 327° .

By means of empirical Equation 6 we can also plot the vapor-pressure curve which would be obtained at 30° , using for the purpose the values of a and c which give the e. m. f. curve at that temperature, according to Equation 7. The result is seen in the broken curve in Fig. 1. The difference between the curve at high and at low temperature, as would be expected, is in the direction of greater solvation at the lower temperature. The substantial agreement as to type justifies the belief that we now have at both temperatures, very accurate information on both the vapor pressure and the free energy of dilution of thallium amalgams.

One more fact remains to be pointed out in connection with the e. m. f. equation. In previous publications objection has been made to the Callendar equation

$$e_{\text{EF}} = RT \ln \frac{c_2}{c_1} + U,$$

where U is the heat of dilution, on the ground that any exact correction

must be made by altering the term $RT \ln c_2/c_1$ so as to make it an exact expression of the free energy of dilution, as is the case with the term we have used,

$$\nu RT = \int n d \ln p.$$

It is hard to see how the integration of this could give any such expression as is found in the Cady equation. It must be noted, however, that, contrary to first impressions, the logarithmic term need not be the only one resulting from the integration of the differential. If the vapor-pressure equation used to connect p and n in making the integration contains an exponential term, as is the case with the van Laar equation (6), then an equation of the Cady type is obtained. It is important to note that the van Laar equation and the Cady equation are equivalent to each other, for the exponent in the van Laar equation is intended as an expression for the partial heat of dilution. From the exhaustive tests of the Cady equation by Richards and his co-workers it is evident that this equation, and therefore the van Laar equation as well, corrects for part, but not all, of the deviation from the simple law of the ideal solution. In fact, it would be rather surprising if these equations were to be found exact, as the correcting term should undoubtedly be a free energy term and not a heat term, the other terms being free energy terms. That this is true of the van Laar equation will be more evident if it is written in the equivalent form,

$$RT \ln p/p_0 = RT \ln N + \Delta \bar{H},$$

where $\Delta \bar{H}$ is the partial molal heat of mixing.

In conclusion, it may be announced that one of us is testing a new equation which promises to form the necessary addition to the previous treatment by means of Raoult's law which will make possible an adequate treatment of the theory of solutions. The new expression uses a work term in place of the heat term, the work being that done by expansion against the internal pressure K , when one mol of a liquid having a molal volume, V , in the pure state is mixed with an infinitely large amount of solution in which its molal fraction is N and its partial molal volume is \bar{V} . The equation may be written either

$$RT \ln \frac{p}{p_0} = RT \ln N + K(\bar{V} - V),$$

or

$$\frac{p}{p_0} = N e^{\frac{K}{RT}(\bar{V} - V)}.$$

Experimental proof of the value and scope of this equation will be deferred till a future publication.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE HYDROGEN- AND HYDROXYL-ION ACTIVITIES OF SOLUTIONS OF HYDROCHLORIC ACID, SODIUM AND POTASSIUM HYDROXIDES IN THE PRESENCE OF NEUTRAL SALTS.

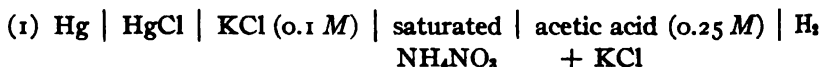
By HERBERT S. HARNED.

Received July 29, 1915.

If the law of mass action, as usually formulated, holds for solutions containing more than one electrolyte, the addition of a salt should decrease the hydrogen-ion concentration of a solution of an acid and the hydroxyl-ion concentration of a solution of a base. There is evidence, however, which seems to indicate that these hydrogen- and hydroxyl-ion concentrations are not decreased but increased by the additions of neutral salts.

From the conductance of solutions of acetic acid containing varying quantities of neutral salts, Arrhenius¹ concluded that the dissociation of the acid was increased. This evidence is not convincing, since so many disturbing factors may influence the results obtained by this method. Arrhenius further found that the addition of potassium chloride to a solution of hydrochloric acid increased its power of inverting cane sugar solutions. He pointed out that this was probably due to the increase in dissociation of the acid. The cause of this phenomenon has not been explained satisfactorily, but the suggestion that the undissociated molecules exert an influence on the velocity of the transformation has afforded the best explanation yet offered.²

If accurate data could be obtained on the hydrogen-ion concentrations of such solutions, a decided advance would be made toward a more complete solution of the problem. In view of the fact that none of the above-mentioned evidence is direct, Loomis and Acree³ attempted to measure the hydrogen-ion concentrations of solutions of acetic acid containing potassium chloride by means of the hydrogen electrode. From the electromotive force of the cells:



and



they obtain the following results:

¹ *Z. physik. Chem.*, **31**, 197 (1899).

² Taylor, *THIS JOURNAL*, **37**, 551 (1915).

³ *Am. Chem. J.*, **46**, 632 (1911).

Mols of KCl per liter.....	0.000	0.05	0.1	0.5	2.06
E. m. f. of (1).....	0.4907	0.4919	0.4927	0.4944	0.4984
E. m. f. of (2).....	0.4930	0.4928	0.4918	0.4894	0.4857

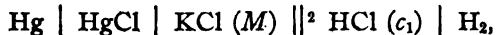
According to the theory of this cell, an increase in electromotive force indicates a decrease in the hydrogen-ion concentration, if the change in electromotive force is produced solely at the contact of the molecular hydrogen and its ions. There is, however, an electromotive force produced at the boundary of the acetic acid and contact solutions, which, as shown by the above results, changes on the addition of potassium chloride. When ammonium nitrate is used as a contact substance, the electromotive force rises on the addition of potassium chloride; when a saturated solution of potassium chloride is used, the electromotive force falls. Of the two series of results obtained by Loomis and Acree, the one in which potassium chloride was used as a contact substance is the more reliable, for the reason that saturated potassium chloride was shown by them to be a better solution for the elimination of liquid potential than saturated ammonium nitrate.¹ If this second series be taken to represent approximately the change in electromotive force of the hydrogen electrode, the hydrogen-ion concentration of the acid has been increased considerably by the addition of potassium chloride.

In these measurements it is obvious that, under all conditions, there will be an effect due to mass action which will tend to decrease the hydrogen-ion concentration; secondly, liquid potential at the solution surfaces will influence the electromotive force of the cell; and thirdly, there may be an increase in hydrogen-ion concentration independent of mass action and liquid potential.

In this investigation, the hydrogen electrode was used in determining the change in hydrogen-ion concentration in solutions of hydrochloric acid, potassium and sodium hydroxides on the addition of different quantities of neutral salts. It was known that the change in liquid potential would be a troublesome factor in these determinations, but it was thought that some light might possibly be thrown on this source of error.

General Theory.

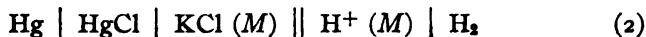
The original formula for the electromotive force of a cell of the type



as given by Nernst was

$$E = E_0 + 0.0591 \log 1/c_1, \quad (1)$$

where E is the observed electromotive force, E_0 is the electromotive force of the cell



¹ See also Bjerrum, *Z. physik. Chem.*, 53, 428 (1905).

² Double line indicates that liquid potential has been eliminated.

and c_1 is the concentration of the hydrogen ions at the hydrogen surface in (1). Lewis¹ has pointed out that the function c_1 , calculated according to this formula, is not equal to the concentration of the ion in solutions which are at all concentrated. For this reason he differentiates this function from the concentration, uses the term activity, and designates it by the symbol a_1 . This function equals the concentration in infinitely dilute solution. Since this investigation is a study of the variation of the value of this function, the term activity of the hydrogen ion will be used. The formula for the cell becomes

$$E = E_0 - 0.0591 \log a_1. \quad (3)$$

Now, suppose that on the addition of salt to the acid, the electromotive force of the cell changes from E to E_1 , then the activity must have changed from a_1 to a_2 , and, for the second cell, the following relation holds:

$$E_1 = E_0 - 0.0591 \log a_2 \quad (4)$$

Subtracting (4) from (3), the following equation is obtained:

$$E - E_1 = -0.0591 \log a_1 + 0.0591 \log a_2 = -0.0591 \log a_1/a_2 \quad (5)$$

Thus, if the activity of the hydrogen ion in the solution of the acid is known, then from the change in electromotive force, if liquid potential has been eliminated, the activity in the presence of the neutral salt can be calculated.

Preparation of Materials.

It is particularly important in making measurements with cells of this type to have the mercury and the calomel in the calomel electrode pure. In order to insure this, mercury, after having been washed ten times by dropping through a solution of nitric acid containing mercurous nitrate, was four times distilled. Samples from two successive distillations gave no difference in electromotive force when tested by the method proposed by Hulett.²

To prepare the calomel, this mercury was dissolved in distilled nitric acid, and, after dilution, the solution was precipitated by redistilled hydrochloric acid and washed free from acid by conductivity water.

The sodium, potassium and calcium chlorides were prepared by three reprecipitations of "analyzed" materials by passing hydrochloric acid gas over the aqueous solutions contained in platinum dishes in the apparatus designed by Lukens.³ The sodium and potassium chlorides were fused in platinum, the calcium chloride was dried at 300°. These were kept in tightly stoppered bottles in a desiccator.

The strontium and barium chlorides were purified by recrystallization from redistilled water. The hydrated salts were used.

¹ THIS JOURNAL, 35, 1 (1913).

² *Phys. Rev.*, 21, 388 (1905).

³ THIS JOURNAL, 35, 1472 (1913).

Lithium chloride was dissolved in water and the carbonate was precipitated by a solution of ammonium carbonate. The carbonate was washed with a solution of ammonium carbonate until free from chlorides, then dissolved in nitric acid. The solution was evaporated until a large portion of the nitrate separated. The latter was three times recrystallized and finally converted to the chloride by passing hydrochloric acid gas over its solution in a quartz dish. The precipitated chloride was centrifuged out, redissolved, then reprecipitated by hydrochloric acid gas. The fused salt was used.

A pure grade of potassium and sodium hydroxide was used as purchased.

Sodium bromide was three times recrystallized from redistilled water.

All the water used was redistilled, first, from a solution of alkaline permanganate; secondly, from sulfuric acid, through a block tin condenser.

Apparatus.

For the measurements in which a saturated potassium chloride solution was used as a contact between the hydrogen and calomel electrodes, the cell (Fig. 1), a modified form of that used by Wilsmore,¹ was found to be easily reproducible to within a few tenths of a millivolt. The hydrogen, prepared electrolytically, was bubbled regularly through the solution contained in A, and thence through the hydrogen electrode vessel B. It was allowed to escape through the trap F which was open to the atmosphere. By passing the gas through the same solution in A as in B, it becomes saturated with the vapor of the solution, thus preventing evaporation of the solution in B.

A number of electrodes made of sheet platinum covered with a thick coating of platinum black, were employed, prepared according to Loomis and Acree.² All the precautions on preparing and cleaning the electrodes were taken.

The hydrogen electrode was connected with the calomel electrode through a saturated solution of potassium chloride contained in C. Between measurements, C was lowered after the stopcocks K and L were closed. In this way, the solution in C was kept separated from the solutions in the hydrogen and calomel electrodes. After each measurement the tubes TT were washed out by means of the solutions contained in DD. In this way any contact solution was prevented from entering the hydrogen electrode and fresh surfaces of contact between all the solutions were maintained.

Connection with the mercury in the calomel electrode was made by means of a platinum wire sealed in the end of tube M. The calomel paste, washed with a solution of potassium chloride of the desired strength,

¹ *Z. physik. Chem.*, 35, 296 (1900).

² *Am. Chem. J.*, 46, 585 (1911).

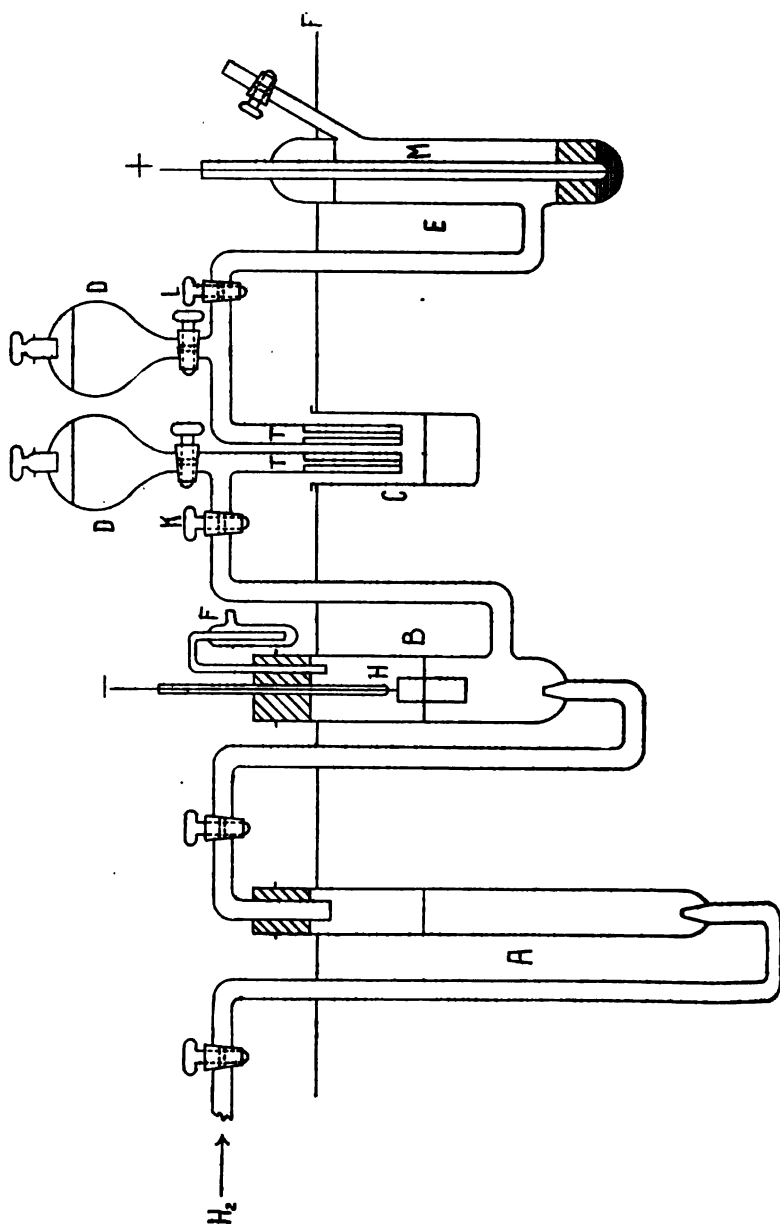


Fig. 1.

was introduced and simply shaken with the mercury as directed by Lewis.¹

The whole cell was immersed in a thermostat up to the level P. All the measurements were carried out at a temperature of $25.00 \pm 0.01^\circ$.

The electromotive force of this cell was obtained by means of a Wolff 15,000 ohm potentiometer and a suitable galvanometer.

Measurements of the Acid-Salt System.

Each observation required from four to five hours before constancy was assured. The following results made with the cell



will show the constancy obtainable with the apparatus used. These particular measurements were made to test the reproducibility of the platinized sheet platinum electrodes. To each measurement it is necessary to apply the correction, $RT/(2F \ln 1/p)$ for the pressure of the hydrogen, where p equals the pressure of the gas in atmospheres. This is less than the atmospheric pressure by the vapor pressure of the solution. At 25° , the vapor pressure of water is 23.5 mm. This, expressed in atmospheres, subtracted from the barometric pressure, gave the value of p which was used in the above formula. Although the vapor pressure of the solutions in the hydrogen electrode were less than that of water, the error introduced by this substitution was less than the error of experiment.

TABLE I.—COMPARISON OF ELECTRODES.

Time. (Hours.)	E. M. F. (Obs.)	Corr. for the pres- sure of H.	E. M. F. (Corr.)
No. 1			
2	0.34893
3	0.34912
4	0.34916	0.00032	0.34948
No. 2			
2	0.34899
3	0.34907
4	0.34904	0.00036	0.34940
No. 3			
4	0.34921	0.00040	0.34961
No. 4			
4	0.34920	0.00040	0.34960

Mean, 0.34952

From the first two of these results it is seen that the cell reaches a value constant within 0.05 of a millivolt in four hours. All observations were carried out in the same manner and were only accepted when this constancy was obtained. The final results are seen to vary in the fourth place. Therefore, in what follows, they will be expressed to 0.1 millivolt only.

¹ THIS JOURNAL, 31, 355 (1909).

The variations in the electromotive force of this cell on the addition of neutral salts to the hydrochloric acid in the hydrogen electrode are given in Table II.

TABLE II.

Conc. of salt in mols per l.	R. M. F. (Obs.)		Corr. for pressure of H.	R. M. F. (Corr.)
No. 1. Hg HgCl KCl (M) sat. KCl KCl in HCl (0.1 M) H ₂ .				
0.000	0.3495
0.1375	0.3488		0.0004	0.3492
0.275	0.3487		0.0003	0.3490
0.530	0.3479		0.0004	0.3483
0.825	0.3470		0.0004	0.3474
1.100	0.3455		0.0004	0.3459
1.376	0.3439		0.0004	0.3443
3.134	0.3322		0.0004	0.3326
No. 2. Hg HgCl KCl (M) sat. KCl NaCl in HCl (0.1 M) H ₂ .				
0.000	0.3495
0.186	0.3480		0.0004	0.3484
0.562	0.3451		0.0003	0.3454
0.606	0.3450		0.0004	0.3454
1.488	0.3363		0.0004	0.3367
No. 3. Hg HgCl KCl (M) sat. KCl BaCl ₂ ·2H ₂ O in HCl (0.1 M) H ₂ .				
0.000	0.3495
0.092	0.3479		0.0004	0.3483
0.185	0.3464		0.0003	0.3467
0.277	0.3448		0.0003	0.3451
0.461	0.3410		0.0004	0.3414
0.500	0.3402		0.0004	0.3406
No. 4. Hg HgCl KCl (M) saturated KCl SrCl ₂ ·6H ₂ O in HCl (0.1 M) H ₂ .				
0.000	0.3495
0.185	0.3464		0.0003	0.3467
0.093	0.3482		0.0003	0.3485
0.278	0.3453		0.0004	0.3457
0.324	0.3440		0.0004	0.3444
0.463	0.3413		0.0004	0.3417
No. 5. Hg HgCl KCl (M) saturated KCl CaCl ₂ in HCl (0.1 M) H ₂ .				
0.000	0.3495
0.132	0.3464		0.0004	0.3468
0.260	0.3442		0.0004	0.3446
0.396	0.3413		0.0004	0.3417
0.530	0.3385		0.0004	0.3389
0.795	0.3322		0.0003	0.3325
No. 6. Hg HgCl KCl (0.1 M) saturated KCl LiCl in HCl (0.1 M) H ₂ .				
0.000	0.4004
0.359	0.3962		0.0006	0.3968
0.717	0.3931		0.0003	0.3934
1.077	0.3876		0.0006	0.3882
1.435	0.3834		0.0004	0.3838

TABLE II (continued).

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 7. Hg HgCl KCl (0.1 M) saturated KCl NaBr in HCl (0.1 M) H ₂ .			
0.000	0.4004
0.285	0.3980	0.0004	0.3984
0.855	0.3942	0.0003	0.3945
1.426	0.3897	0.0003	0.3900
No. 8. Hg HgCl KCl (0.1 M) saturated KCl mannite in HCl (0.1 M) H ₂ .			
0.000	0.4004
0.116	0.4000	0.0004	0.4004
0.232	0.3998	0.0004	0.4002
0.464	0.3995	0.0004	0.3999
0.580	0.3997	0.0004	0.4001

When the solution of lithium chloride in hydrochloric acid was measured, a 0.1 M calomel electrode was used in order to compare the results obtained by this cell with those obtained by Loomis and Acree. For the cell



three different electrodes gave the following values:

E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
0.3999	0.0003	0.4002
0.4001	0.0003	0.4004
0.4001	0.0004	0.4005

Mean, 0.4004

As a mean of four measurements of the same cell, Loomis and Acree obtained 0.4001. This concordance is good confirmation of the accuracy of the apparatus employed in this series of measurements.

In Experiments 1 to 6, all the salts introduced into the acid possess an ion common with the anion of the acid. To introduce a salt which did not possess a common ion, sodium nitrate was tried, but this was found to be reduced to ammonia by molecular hydrogen in the presence of platinum black. Sodium bromide gave values under No. 7.

Finally, in order to have an example of the action of a nonelectrolyte, mannite was introduced into the acid. The results are given under No. 8.

These results can best be interpreted from the plots (Fig. 2). Here, change in electromotive force in volts is plotted against the concentration of the salt in the acid expressed in gram equivalents per liter. A drop in the plot indicates a drop of potential.

The first fact of importance to be observed from these results is that in every case there is a fall in electromotive force while the mass-action effect¹ would tend to increase the electromotive force of the cell owing

¹ As ordinarily understood, where the equilibrium under consideration is assumed to be between the ions and the undissociated molecules and the equilibrium between these and the solvent is not taken into account.

to a decrease in hydrogen-ion activity. Secondly, since in every case the mobility of the anion of the salt is greater than that of the cation, addition of salt will change the liquid potential between the saturated

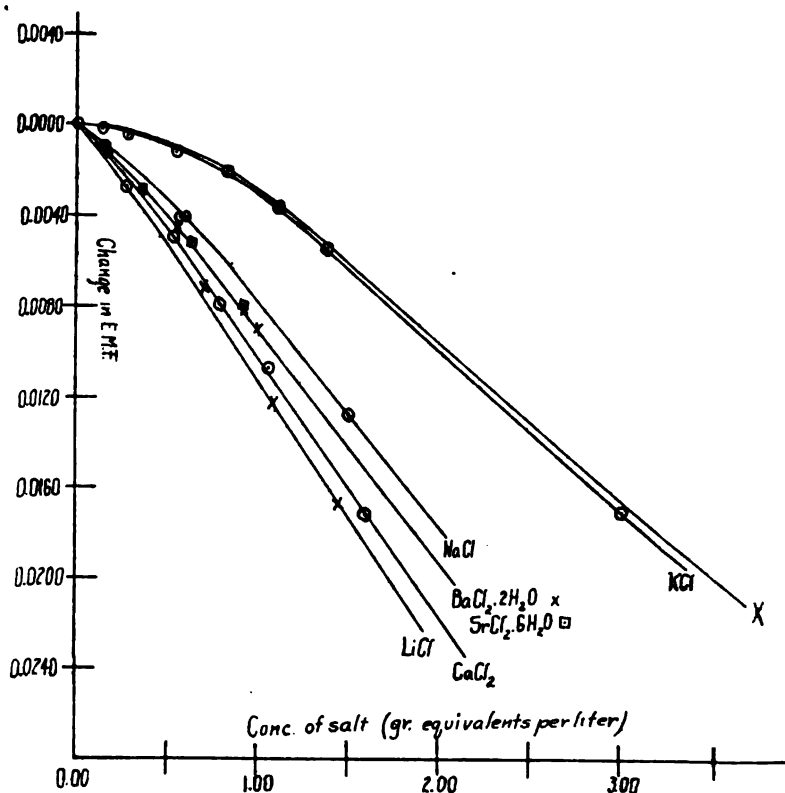


Fig. 2.—HCl-salt solution mixtures.

potassium chloride solution and the hydrochloric acid-salt solution in direction which will decrease the electromotive force of the cell. The question thus arises whether this drop in potential is entirely due to liquid potential.

A study of the distribution of these curves will afford evidence that the latter is not the case, but that a decrease in electromotive force of the hydrogen electrode (0.1 *M* HCl) is produced by the addition of neutral salts. Fig. 3 gives the conductance curves of the alkali and alkaline earth chlorides.¹ Here, equivalent conductance is plotted against concentration in gram equivalents per liter. It is obvious that there is an analogy between the distribution of these plots with those given in Fig. 2. The molecular conductance is a function of the degree of ionization and

¹ From the data of Kohlrausch (18°).

ic mobilities. Therefore, the difference between these conductance
 its for the different salts is a function of the degrees of dissociation
 & the difference of the mobilities of the cations, since in every case
 anions are the same. In like manner, the differences in the electro-
 tive force plots (Fig. 2) will be a function of the degrees of dissocia-
 n and the differences between mobilities of the cation. The meaning
 these facts is obvious, for it is the difference in the ionic mobilities

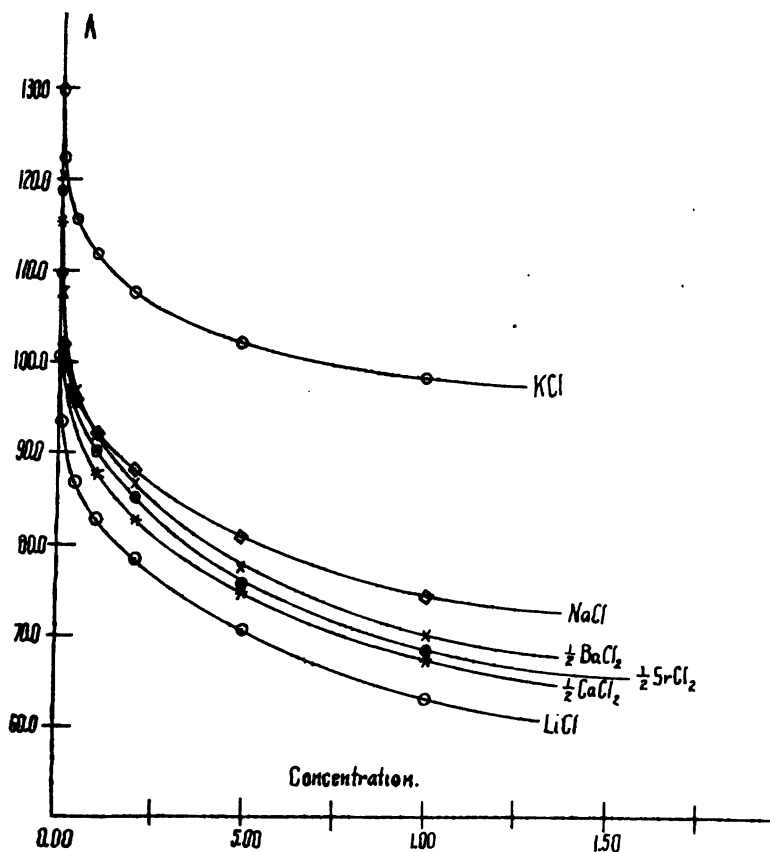


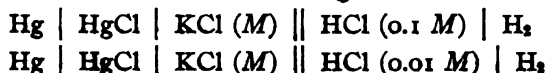
Fig. 3.—Conductance plots. 18°.

h gives rise to the production of a liquid potential between two solu-
 surfaces. This interpretation is borne out by the experimental
 its. The mobility of the potassium ion¹ is 64.5, that of the chlorine
 is 5.5. These are nearly the same, and, for this reason the addition
 potassium chloride would be expected to produce only a slight change in
 Noyes and Falk, *THIS JOURNAL*, 34, 479 (1912). The mobility of the lithium
 at 25° is not given by Noyes and Falk. For this reason, the values at 18° are used
 Since ratios are desired, these values are satisfactory for the present discussion.

liquid potential. The mobilities of the sodium and lithium ions, 43.45 and 33.3, respectively, are less than that of the potassium ion and hence should give a greater change in liquid potential than does potassium chloride. This is found to be the case. Furthermore, since from the conductance data the degrees of dissociation of these chlorides are nearly the same, the differences in change of liquid potential produced by them should be in the ratios of their ionic mobilities. Thus, the difference between the ionic mobilities of the potassium and sodium ions is 21.1, between the sodium and lithium 10.1. The ratio of the difference between the potassium chloride and sodium chloride plots and the sodium and lithium chloride plots (Fig. 2) is found by experiment to be approximately 2 to 1. Since this ratio holds, it seems that the mass-action effects of these chlorides are approximately identical.

As a result of this evidence there is fair reason to assume that the differences in the distribution of these curves are entirely due to differences in change of liquid potential. The curve for potassium chloride now becomes extremely interesting, for, since the ionic mobilities in this salt are so nearly the same, practically no change in liquid potential would be expected. This argues for the conclusion that there is a third influence operating here, opposite in its action to the effect of mass action as ordinarily understood and influencing the electromotive force of the cell in the same direction as the change of liquid potential. Furthermore, if the differences in the distribution of these plots is, as has been assumed above, due entirely to differences in liquid potential, a curve of zero liquid potential can be predicted. This would be a plot produced by a salt which would yield ions having identical mobilities. If the above assumptions are true, X will represent the change in electromotive force of the hydrogen electrode produced by the addition of salts to 0.1 *M* hydrochloric acid.

The following calculations made from plot X by means of Formula 5 will show the increase in activity of the hydrogen ion in a 0.1 *M* solution of hydrochloric acid on the addition of a neutral salt. First, however, it is necessary to determine the hydrogen-ion activity in 0.1 *M* hydrochloric acid. From the most recent and accurate work of the hydrogen electrode, Lewis¹ has obtained 0.3460 and 0.3980, respectively, for the electromotive forces of the following cells:



Furthermore, he gives 0.92 as the corrected value of the degree of dissociation of 0.01 *M* HCl. On the assumption that in 0.01 *M* solution the activity equals the concentration, the activity of the hydrogen ion

¹ THIS JOURNAL, 36, 1969 (1914).

in 0.1 *M* solution can be calculated by Equation 5. From the above data, it is found that the cell



has an electromotive force of 0.0520 volt. Hence,

$$0.0520 = 0.0591 \log a/0.0092$$

and *a* becomes 0.0698.

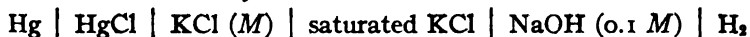
TABLE III.—HYDROGEN-ION ACTIVITY FROM PLOT X.

Conc. of salt.....	0.000	0.500	1.000	1.500	2.000	2.500	3.000
<i>a</i>	0.0698	0.0720	0.0778	0.0882	0.1002	0.1149	0.1323

From these data it is seen that the hydrogen-ion activity has been nearly doubled by the presence of a salt of 3 *M* concentration. Observation of the calcium, strontium, and barium chloride plots will show that the effect of hydration is small. It is interesting to note that the excess of four molecules of water of crystallization of the strontium chloride over those of the barium chloride dilutes the solution sufficiently to render their plots identical. According to the conductance curves, the strontium chloride plot should lie between the calcium and barium chloride plots.

The Hydroxide-Salt System.

From these experiments it follows that the addition of neutral salts to a 0.1 *M* hydrochloric acid solution increases the hydrogen-ion activity of the solution. Whether the hydroxyl-ion activity of solutions of sodium and potassium hydroxides is increased or decreased by the addition of neutral salts, is shown by the variations of the cells



on the addition of neutral salts to the hydroxides in the hydrogen electrode as can be seen in the results of Table IV.

TABLE IV.

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 1. Hg HgCl KCl (<i>M</i>) saturated KCl KCl in NaOH (0.1 <i>M</i>) H ₂ .			
0.000	1.0412	0.0004	1.0416
0.386	1.0413	0.0003	1.0416
1.157	1.0409	0.0004	1.0413
1.928	1.0425	0.0004	1.0429
No. 2. Hg HgCl KCl (<i>M</i>) saturated KCl NaCl in NaOH (0.1 <i>M</i>) H ₂ .			
0.000	1.0416
0.467	1.0368	0.0004	1.0372
0.926	1.0341	0.0004	1.0345
1.402	1.0318	0.0004	1.0322
1.869	1.0305	0.0004	1.0309
2.337	1.0292	0.0004	1.0296

TABLE IV (continued).

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 3. Hg HgCl KCl (0.1 M) saturated KCl KCl in KOH (0.1 M) H ₂			
0.000 ¹	1.0941	0.0004	1.0945
0.000 ¹	1.0940	0.0003	1.0943
0.000 ¹	1.0943	0.0003	1.0946
0.259	1.0929	0.0003	1.0932
0.518	1.0927	0.0003	1.0930
1.295	1.0933	0.0003	1.0936
2.027	1.0945	0.0004	1.0949
2.978	1.0986	0.0003	1.0989
No. 4. Hg HgCl KCl (0.1 M) saturated KCl NaCl in KOH (0.1 M) H ₂			
0.000	1.0945
0.346	1.0879	0.0003	1.0882
0.692	1.0857	0.0004	1.0861
1.038	1.0838	0.0004	1.0842
1.728	1.0814	0.0004	1.0818
No. 5. Hg HgCl KCl (0.1 M) saturated KCl LiCl in KOH (0.1 M) H ₂			
0.000	1.0945
0.661	1.0803	0.0003	1.0806
1.322	1.0709	0.0003	1.0712
1.983	1.0629	0.0004	1.0633

The plots of these observations are given in Fig. 4. Change in electromotive force of the cell is plotted against the concentration in mols per liter of the salts added. The electromotive forces of the cells when no salts are present in the hydroxides are zero on the scale of ordinates.

In the first place, in the case under immediate discussion, the change in liquid potential and mass-action effect increases the electromotive forces of the cells. The plots of potassium chloride in both the sodium and potassium hydroxides clearly show that there is an increase in electromotive force which indicates an increase in hydroxyl-ion concentration.

There is, however, a striking difference between the distribution of the plots in Fig. 2 and Fig. 4. In the acid system, the difference in the changes in electromotive force produced by the different salts is much less than the corresponding differences in the hydroxide system. This is due, in part at least, to the differences in magnitude of the liquid potentials. A comparison of the liquid surfaces under discussion will serve to explain this difference. In the acid system, the change in liquid potential will be produced at the liquid surface

MeX in HCl (0.1 M) | saturated KCl.

On the addition of salt, the acid solution will become positively charged to the saturated potassium chloride solution, owing to the fact that, in

¹ Carried out with three different electrodes.

every case, the anion has a greater mobility than the cation. At the same time, we have found that the activity of the hydrogen ion has been increased. This will tend to charge the saturated potassium chloride solution positive to the acid solution, owing to the relatively high mobility

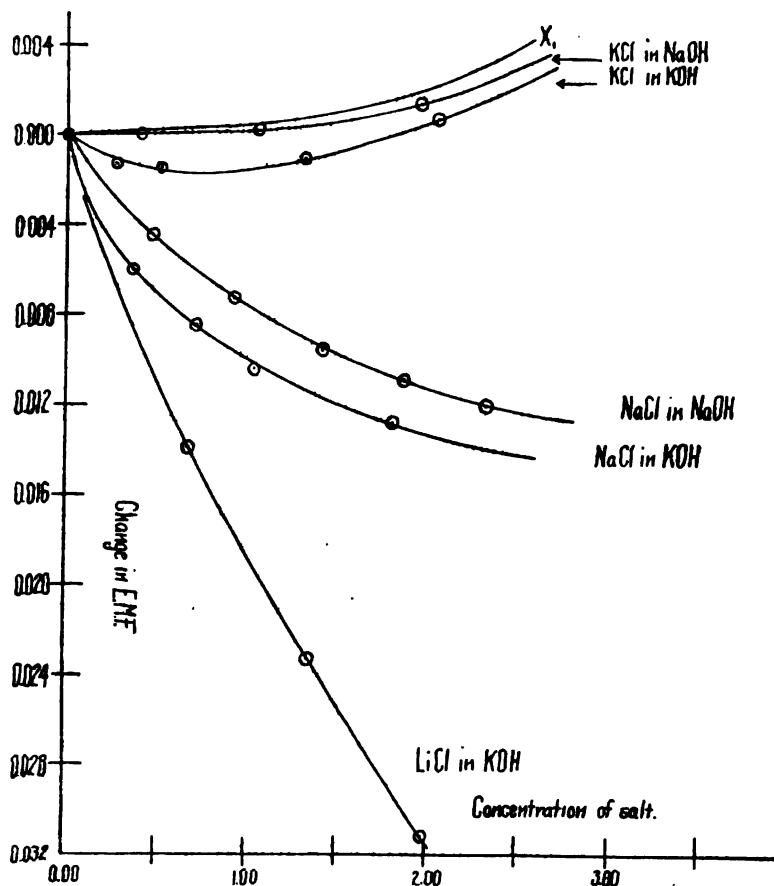
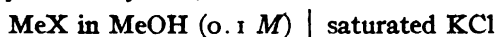


Fig. 4.

of the hydrogen ion. Thus, there is set up a liquid potential which tends to oppose that set up by the salt. Therefore, the influence of this increase in hydrogen ion activity on the liquid potential in the acid system will cause the plots of the different salts to fall close together.

Now in the hydroxide system, the surface



will produce the liquid potential. As before, the influence of the addition of salt will be to decrease the electromotive force of the cell. But the hydroxyl-ion concentration has increased, and this will change the

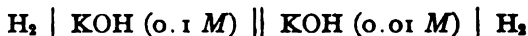
liquid potential, and, like the salt, it will tend to increase the negative charge on the saturated potassium chloride solution, owing to the high mobility of the hydroxyl ion. The total effect will be to spread the plots in Fig. 4.

The wide differences between these plots are probably not entirely due to these differences in liquid potentials. Since, in a solution containing lithium chloride and potassium hydroxide, there will be an equilibrium between the ions and the undissociated molecules, and, since the best evidence shows that the degree of dissociation of lithium hydroxide is less than that of sodium or potassium hydroxides, a difference in mass-action effects would be expected. This may act in such a way as to cause the plots to spread.

These plots afford excellent evidence that there is an increase in electromotive force produced by the presence of neutral salts in hydroxide solutions, according to which the hydroxyl-ion activity of the solution will be increased.

It can be assumed, as in the case of the acid systems, that the differences in the plots of the different salts, with the exception of the lithium chloride plot, is due only to the differences in liquid potential and mass action, and from the above data, X_1 can be plotted, which represents the change in electromotive force of the hydrogen electrode produced by the addition of salts to 0.1 *M* sodium hydroxide.

Table V gives the increase in hydroxyl-ion activity due to the presence of neutral salts according to curve X_1 . From the recent accurate investigations of Lewis and Lorentz, and Bohi,¹ the value of the cell



is 0.0562 volt. From the assumption that in 0.01 *M* potassium hydroxide, the hydroxyl-ion activity is 0.0092, the hydroxyl-ion activity in 0.1 *M* solution can be computed by Equation 5 as follows:

$$0.0562 = 0.05915 \log a/0.0092$$

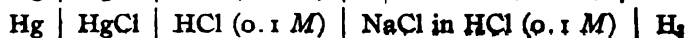
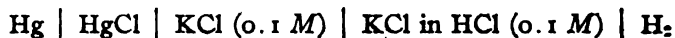
Thus a equals 0.0822.

TABLE V.—HYDROXYL-ION ACTIVITY FROM PLOT X_1 .

Conc. of salt.....	0.000	0.500	1.000	1.500	2.000	2.500	3.000
a	0.0822	0.0828	0.0835	0.0855	0.0892	0.0961	0.1071

The Liquid Potential Effect.

It was thought that a further investigation of the liquid potentials might contribute evidence in confirmation of the positions of the plots for zero liquid potential, namely, X and X_1 (Figs. 2 and 4). To this end, measurements of the cells



¹ *Z. physik. Chem.*, 66, 733 (1909).

were made. In this series of observations, it was found that the cell used in the previous experiments gave results which did not attain the desired constancy even after a period of ten hours. In order to overcome this difficulty, another cell was set up which differed only in the slightest particulars from that used by Loomis and Acree. Even then, the constancy obtained by using a saturated potassium chloride solution as a contact was not reached when the concentration of the salt in acid was greater than 0.5 *M*. In all cases, however, constancy was attained within 0.2 of a millivolt. Table VI shows the results.

TABLE VI.

Conc. of salt.	E. M. F. (Obs.)		Corr. for pressure of H.	E. M. F. (Corr.)	
No. 1.	Hg HgCl KCl (0.1 <i>M</i>) KCl in HCl (0.1 <i>M</i>) H ₂ .				
0.000		0.42704 ¹	0.00034		0.4274
0.095		0.4230	0.0003		0.4233
0.286		0.4161	0.0003		0.4164
0.477		0.4123	0.0003		0.4126
0.953		0.4085	0.0004		0.4089
2.358		0.3968	0.0003		0.3971
3.423		0.3861	0.0002		0.3863
No. 2.	Hg HgCl HCl (0.1 <i>M</i>) NaCl in HCl (0.1 <i>M</i>) H ₂ .				
0.000		0.3987	0.0004		0.3991 ²
0.014		0.3983	0.0003		0.3986
0.028		0.3975	0.0003		0.3978
0.070		0.3975	0.0003		0.3978
0.141		0.3963	0.0006		0.3969
0.423		0.3947	0.0003		0.3950
0.705		0.3922	0.0003		0.3925
1.062		0.3890	0.0002		0.3892
1.133		0.3879	0.0003		0.3882
1.416		0.3843	0.0004		0.3847

A comparison of the plots of these results with those obtained when a contact solution was used are given in Figs. 5 and 6. With Plot B (Fig. 5) there is a definite liquid potential at the start between the 0.1 *M* potassium chloride solution and the 0.1 *M* hydrochloric acid. This, according to Lewis and Sargent,³ amounts to 0.0284 volt. On the addition of potassium chloride to the acid, this is decreased. The fact of most importance to be derived from Plots A and B (Fig. 5) is the large difference in the change in e. m. f. between them. This wide discrepancy affords an excellent means of testing the liquid potential formula.

The former experiments have indicated that the plots *X* and *X*₁ (Figs. 2 and 4) represent the changes in e. m. f. produced at the hydrogen elec-

¹ This agrees with the value 0.4270 obtained by Bjerrum (*Z. physik. Chem.*, **53**, 428 (1905)).

² The latest value of Sebastian (Lewis, *THIS JOURNAL*, **36**, 1968 (1914)) is 0.3990.

³ *THIS JOURNAL*, **33**, 306 (1911).

trode alone. In order to confirm the assumptions made in regard to these experiments, the values of a few of these liquid potentials were calculated and deducted from the original results. After the liquid potential has been eliminated by this method, the plots of the results may be compared to Plots X and X_1 .

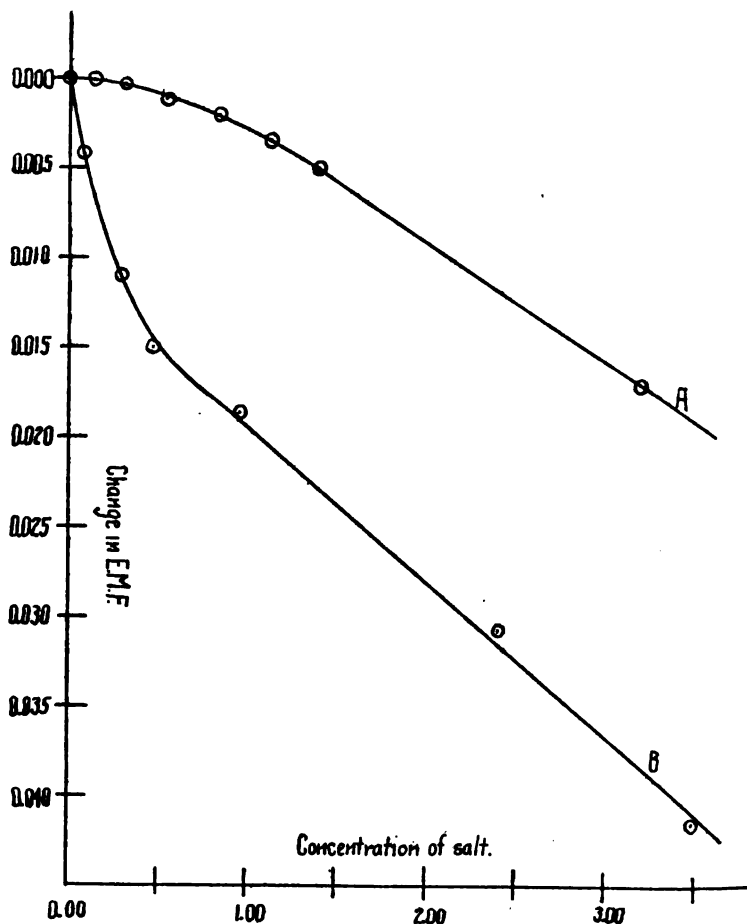


Fig. 5.

Planck¹ has deduced a general differential equation for the liquid potential between two solutions containing univalent ions. On the assumption that the simple gas equation holds for solutions, and that the ideal diffusion laws hold, this equation can be integrated, and gives the following:

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} \times \frac{C_2 - \xi C_1}{\xi C_2 - C_1} = \frac{\log C_2/C_1 - \log \xi}{\log C_2/C_1 + \log \xi}$$

¹ *Wied. Ann.*, 39, 161 (1890); 40, 561 (1890).

where U_1 equals the product of the mobilities of the cations in the dilute solution and the concentration of the ions; U_2 the same in the concentrated solution; V_1 , the product of the mobility and the concentration of the anions in the dilute solution; V_2 , the same for the anions in the concentrated solution. C_1 equals the total ionic concentration in the dilute solution; C_2 the total ionic concentration in the concentrated solution. From the function ξ , the liquid potential E can be calculated by the formula

$$E = 0.0591 \log \xi.$$

Although this equation was cumbersome, and could only be solved by a method of approximation, it was the only one which was general enough for the calculation of the complex liquid potentials under consideration. Furthermore, it was realized that it was only accurate to within a few millivolts when applied to solutions of concentration above 0.1 M . However, it was the best that could be found for the present purpose, and, as will be seen, affords interesting confirmation of the experimental results.

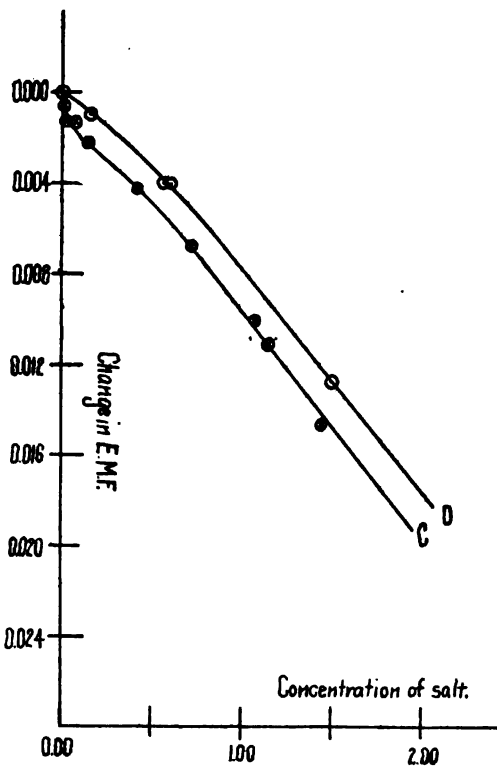


Fig. 6.

In the use of this equation, the following assumptions were made:

1. That the degree of dissociation, α , obtained from conductance measurements, represents the correct value.
2. That, in solutions containing both salt and acid or hydroxide, the ions act independently. U_2 , V_2 , U_1 , V_1 represent, then, the mean mobility of the ions times their total concentration in the concentrated and dilute solutions, respectively.

In Table VII (1) is the liquid potential calculated by the Planck formula, (2) is the change in liquid potential produced by the addition of the salt to the solution.

These calculated changes in electromotive force are eliminated from those actually observed, and the resulting values are plotted in Fig. 7

TABLE VII.

Conc. of salt.	(1).	(2).	(1).	(2).
No. 1. KCl in HCl (0.1 M) KCl (0.1 M).		No. 3. NaCl in HCl (0.1 M) HCl (0.1 M).		
0.000	0.0267 ¹	0.0000
0.10	0.0201	-0.0066	-0.0018	-0.0018
0.50	0.0105	-0.0162	-0.0059	-0.0059
1.00	0.0099	-0.0168	-0.0088	-0.0088
2.00	0.0095	-0.0172	-0.0092	-0.0092
No. 2. KCl in HCl (0.1 M) KCl (4.16 M).		No. 4. KCl in NaOH (0.1 M) KCl (4.16 M).		
0.000	0.0052	-0.0006
0.50	0.0025	-0.0027	-0.0009	-0.0005
1.00	0.0021	-0.0031	-0.0010	-0.0004
2.00	0.0019	-0.0033	-0.0011	-0.0005

along with the plots X and X₁.² First, it is to be noticed that the plots A and B (Fig. 5) have been brought close together and fall near Plot C in Fig. 6. For example, in the presence of 2 M salt, there is a difference of 0.005 volt. Before the correction for liquid potential was made, the difference was 0.019 volt. Furthermore, the acid curves fall around X. It is realized that the agreement between the calculated and the ob-

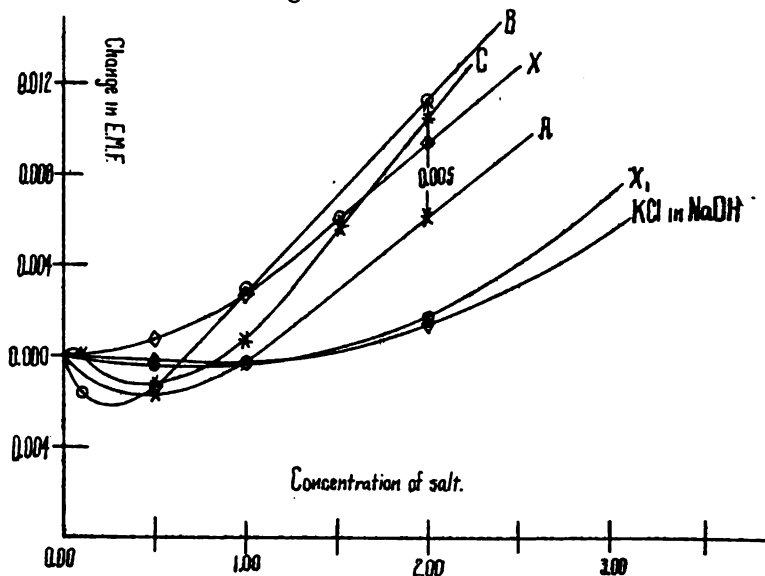


Fig. 7.

¹ The value obtained by Lewis and Sargent's formula (*loc. cit.*) is 0.0284. The value calculated by Planck's formula is used in these calculations, for, since the change in e. m. f. is the important factor, it was thought best to use the same equation for all calculations.

² In Fig. 7, a drop in potential for the acid plots is indicated by a rise in the curve; a rise in potential for the hydroxide plots corresponds to a rise in the curve. In this way, the relative magnitudes of X and X₁ can be compared.

served results is not all that may be desired, but the evidence thus obtained contributes in confirming the position of X and X₁.

The Mass-Action Effect.

It is of interest to notice the similarity of the plots of sodium chloride and bromide in hydrochloric acid solution (Fig. 8). Up to the salt con-

centration of 0.65 M, these plots are almost identical; beyond this, there is a slight deviation. Since the mobilities of the chlorine ion and bromine ion only differ slightly, a very small difference in liquid potential would be expected. Also, the plots of potassium chloride in potassium and sodium hydroxides are nearly identical, as are those of sodium chloride in these two hydroxides. It appears that the presence in the salt of an ion common with the acid or the base causes no greater mass-action effect than when no common ion is present. This raises the question as to whether this behavior is in full theoretical accord with the law of mass action as usually applied. In the following deductions, the action of sodium

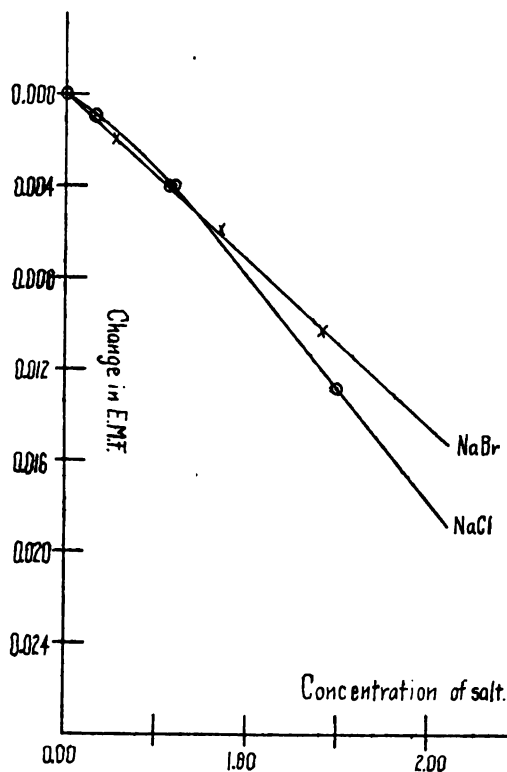


Fig. 8.

chloride and bromide on the hydrogen-ion concentration¹ of hydrochloric acid is investigated. These examples will serve as types:

Case I.—The acid and salt have no ion in common. In this the sodium bromide hydrochloric acid solution, four equilibria must be considered, namely, those between the ions and the undissociated hydrochloric acid, hydrobromic acid, sodium chloride and sodium bromide. The assumption that the equilibrium constants of these four substances are equal is in good accord with the experimental results. This leads to the following set of equations:

$$K = xy/a = xv/b = yz/c = zv/d \quad (6)$$

¹ Concentrations are used instead of activities in the following mass-action calculations.

where $x = [\text{H}]$, $y = [\text{Cl}]$, $z = [\text{Na}]$, $v = [\text{Br}]$, $a = [\text{HCl}]$, $b = [\text{HBr}]$, $c = [\text{NaCl}]$, and $d = [\text{NaBr}]$.

Now, let n equal the equivalent acidity, m the concentration of salt added in moles per liter. Then

$$\left. \begin{aligned} x + a + b &= n \\ y + a + c &= n \\ z + c + d &= m \\ v + b + d &= m \end{aligned} \right\} \quad (7)$$

Eliminating a, b, c, d from Equations 6 and 7, the following set of equations is obtained:

$$\left. \begin{aligned} x + xy/K + xv/K &= n \quad (a) \\ y + xy/K + yz/K &= n \quad (b) \\ z + yz/K + zv/K &= m \quad (c) \\ v + xv/K + zv/K &= m \quad (d) \end{aligned} \right\} \quad (8)$$

By dividing (b) by (d), we obtain $v/y = m/n$. (9)

By dividing (a) by (c), we obtain $z/x = m/n$. (10)

Furthermore, Equations 8 are symmetrical and hence

$$x = y \text{ and } z = v. \quad (11)$$

Therefore, from (9), (10) and (11), we obtain

$$x^2 [(n + m)/Kn] + x - n = 0. \quad (12)$$

When $m = 0$, α , the degree of dissociation of the acid, equals x/n , $x = \alpha n$. Hence,

$$K = \alpha^2 n / (1 - \alpha).$$

This is the well-known dilution law.

Case II.—The acid and the salt have an ion in common. In this case there will be present only two undissociated molecules, namely, hydrochloric acid and sodium chloride, and, on the assumption that the dissociation constants of these are the same, we obtain

$$K = xy/a = yz/c. \quad (13)$$

Furthermore,

$$\left. \begin{aligned} x + a &= n \quad (3) \\ z + c &= m \quad (2) \\ y + a + c &= m + n \quad (3) \end{aligned} \right\} \quad (14)$$

Hence, $x + z = y$. (15)

Equations 13 and 14 give on the elimination of a and c

$$x + xy/K = n; \quad z + yz/K = m \quad (16)$$

which with (15) give on elimination of y

$$x + x(x + z)/K = n; \quad z + z(x + z)/K = m. \quad (17)$$

Solving for x by direct substitution, the same expression is obtained as in Case I, namely:

$$-n = 0 \quad (12)$$

effects of sodium chloride
identical, if the as-
the substances
of the plots
explanation.

emphasize that a
ally applied, is ob-
odium and potassium
In order to bring out
column 1 represents the
hydrogen-ion concentration
observed hydrogen-ion con-
is the ratio of the calculated
chloride, Kraus and Bray¹ con-
value was used for both the dis-
the salt. 0.092² was taken as the
acid. In obtaining the values in
ratio of the activity to the concentra-
constant.

TABLE VIII.

Calc. Obs.	Conc.	Calc. Cl ⁻	Obs. Cl ⁻	Calc.: Obs.
0.630	0.100	0.058	0.087	0.667
0.430	0.300	0.143	0.244	0.586
0.327	0.600	0.216	0.466	0.464
0.233	1.100	0.259	0.842	0.308
0.136	2.100	0.367	1.472	0.249
0.074	3.100	0.459	2.118	0.216

The following calculations from the conductance
(1) Column 5 gives the concentration of salt, (6) is the
ration calculated by Equation 12, (7) is αC or the
on concentration, and (8) is the ratio of the calculated
values.

nt to show the increasing deviation from the mass-action
ases under discussion.

Summary and Conclusion.

Measurements with the hydrogen electrode, evidence has been
which indicates that the hydrogen-ion activity and concentra-
M hydrochloric acid is increased by the presence of neutral

ence has also been obtained that the hydroxyl-ion activities

¹ JOURNAL, 35, 1412 (1913).
² Heyes and Falk, THIS JOURNAL, 34, 485 (1912).

and concentrations of 0.1 *M* potassium and sodium hydroxides is increased by the addition of neutral salts.

3. Tables for the increase of the hydrogen-ion activity of hydrochloric acid solutions, and the hydroxyl-ion activity of potassium and sodium hydroxide solutions containing neutral salts have been appended.

4. The evidence thus far obtained in the acid-salt system indicates that the increase in activity of the hydrogen ion in the acid differs little for the different salts used in these experiments. This does not appear to hold in the hydroxide-salt system.

5. Calculations made by the Planck formula for liquid potential lend confirmation to the experimental results.

6. The experimental fact that sodium bromide produces the same effect on the hydrogen-ion activity of hydrochloric acid solutions as does sodium chloride has been proved to be in accord with the law of mass action. This is also true of similar cases in the hydroxide-salt systems.

7. If the interpretation of the experimental results as given above is correct, then, in a solution of 0.1 *M* hydrochloric acid, the hydrogen-ion concentration has been increased from 0.092 to 0.1765 *M* by the presence of 3 *M* potassium chloride. This points to the conclusion that the solution acts as if it were contracting, or that the volume of solvent has decreased.

PHILADELPHIA, PA.

[FROM THE LABORATORY OF GAS INVESTIGATION OF THE BUREAU OF MINES.]

THE VAPOR PRESSURES OF ACETYLENE, AMMONIA AND ISOBUTANE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.¹

By G. A. BURRELL AND I. W. ROBERTSON.

Received August 16, 1915.

In this report are shown the vapor pressures of acetylene, ammonia, and isobutane at temperatures below their normal boiling points. The method of procedure is the same as that detailed in previous communications to *THIS JOURNAL* by the authors.² The thermometers were calibrated at two additional points, other than those used by the authors in previous work. These points are the melting points of mercury and ice. Henning³ gives for the melting point of mercury, -38.89° . In calibrating thermometers against this point, the authors carefully purified mercury by the method of Hulett.⁴ About 15 cc. of mercury were placed in a test tube and immersed in the gasoline bath⁵ maintained at a

¹ Published by permission of the Director of the Bureau of Mines.

² *THIS JOURNAL*, 37, 1893 (1915).

³ *Ann. Phys.*, 43, 294 (1913).

⁴ *Phys. Rev.*, 34, 307 (1911).

⁵ See *THIS JOURNAL*, 37, 1893 (1915) (Fig. 1).

temperature of a few degrees below the melting point of the mercury. The bath temperature was next allowed to rise slowly. At the melting point the temperature, of course, became stationary until all of the mercury had melted. Next the mercury was again distilled and the operation repeated with the same results. In the two carefully conducted trials with each thermometer, No. 707 was found to register -38.4 and -38.5° , while No. 504 in the same calibrations read -36.5 and -36.6° . From the values so found, the thermometers were corrected according to the melting point found by Henning.

Preparation of Gases.—Acetylene was prepared by the action of water on calcium carbide. The evolved gas was passed through caustic potash solution and then dried over phosphorus pentoxide. Next it was repeatedly fractionated at the temperature of liquid air to remove air and other gases of high vapor pressure at that temperature and finally fractionated several times at a temperature of -120° to -110° , thereby distilling the acetylene from water vapor or other gases whose vapor pressure is prac-

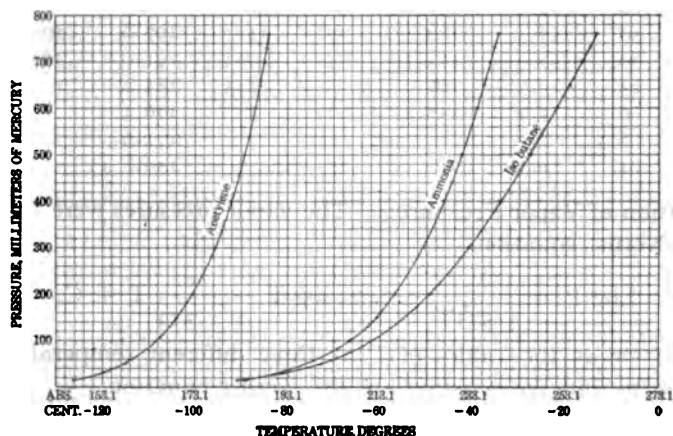


Fig. 1.—Temperature plotted against pressure.

tically nil at that temperature. During the course of the vapor-pressure measurements, part of the acetylene was allowed to evaporate away at different times and the observations were repeated with the remaining portions of the gas. After each introduction of fresh portions of gas into the vapor-pressure bulb, fractionation was performed at the temperature of liquid air to make sure that atmospheric air had not been trapped in the transfer. The above precautions were taken in all the vapor-pressure measurements.

Ammonia was prepared by distilling the gas from c. p. ammonia water.

Isobutane was prepared by the action of isobutyl iodide on a zinc-copper couple.

Both the ammonia and isobutane were purified by repeated distillations at low temperatures.

Table I shows the observed and the calculated vapor pressures for the three gases.

TABLE I.—CALCULATED AND OBSERVED VAPOR PRESSURES.

Acetylene.			Isobutane.			Ammonia.		
Temp. ° Abs.	Pressure, Mm. Hg.		Temp. ° Abs.	Pressure, Mm. Hg.		Temp. ° Abs.	Pressure, Mm. Hg.	
Av. of two.	Obs.	Calc.	Av. of two.	Obs.	Calc.	Av. of two.	Obs.	Calc.
189.1	760	760	259.7	760	760	238.5	760	760
188.6	730	731	258.2	730	731	237.7	730	730
188.0	700	700	256.6	700	694	236.8	700	699
187.2	650	658	254.0	650	651	235.4	650	648
186.1	600	606	251.1	600	598	233.8	600	595
183.6	500	499	245.4	500	500	230.7	500	501
180.8	400	400	239.0	400	400	226.8	400	400
177.3	300	300	232.0	300	305	222.4	300	306
172.5	200	199	211.7	100	115	216.3	200	205
169.1	150	147	200.4	50	58	212.3	150	154
164.9	100	99	192.2	30	32	206.5	100	100
158.0	50	53	182.4	15	15	197.0	50	45
153.2	30	30	174.7	7	7.4	191.0	30	26
147.0	15	15	166.9	3	3.5	184.2	15	14
138.5	6	5.2	158.3	1	1	176.4	7	5.4
132.5	2.5	2.3				171.9	4	3.1
129.9	1	1.58				159.8	1	0.6

Calculation of Vapor Pressures.—The vapor pressures were calculated using the Nernst equation.

$$\log P = \frac{\lambda_0}{4.571T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C.$$

Table II shows the values of P at three different temperatures that were taken to find the constants in the Nernst equation.

TABLE II.

Acetylene.		Isobutane.		Ammonia.	
T°.	P.	T°.	P.	T°.	P.
189.1	760	259.7	760	238.5	760
177.3	300	245.4	500	226.8	400
147.0	15	182.4	15	206.5	100

The equations of the curves are

$$\text{For acetylene, } \log P = -\frac{957.21}{T} + 1.75 \log T - 0.001511T + 3.672$$

$$\text{For isobutane, } \log P = -\frac{1632.661}{T} + 1.75 \log T - 0.0158873T + 9.068$$

$$\text{For ammonia, } \log P = -\frac{1951.72}{T} + 1.75 \log T - 0.015525T + 10.606$$

The straight line curves shown at Fig. 2 were drawn according to an equation which was derived by the method of least squares and which represents the average of all the points.

$$\text{For ammonia the equation is } \log P = -\frac{1371.86}{T} + 8.64.$$

$$\text{For acetylene, } \log P = -\frac{1127.09}{T} + 8.84.$$

$$\text{For isobutane, } \log P = -\frac{1056.25}{T} + 6.98.$$

The heats of evaporation may be calculated from the integrated form of the Clausius-Clapeyron equation

$$\ln P = -\frac{Q}{RT} + \text{const.}$$

Using the values 1371.86, 1127.09 and 1056.25 in this equation, one obtains as the average heats of evaporation over the temperature range studied, in calories per gram-molecule

$$\text{For ammonia: } Q = (1371.86 \times 4.571) = 6271 \text{ calories}$$

$$\text{For acetylene: } Q = (1127.09 \times 4.571) = 5152 \text{ calories}$$

$$\text{For isobutane: } Q = (1056.25 \times 4.571) = 4828 \text{ calories}$$

Brill¹ has determined saturated vapor pressures for ammonia between -80.0° and -33.0° . His results are shown in Table III, along with those of the authors of this paper. The latter were taken from the curve shown at Fig. 1 (drawn to larger scale than shown in Fig. 1).

VAPOR PRESSURES OF AMMONIA AS DETERMINED BY BRILL AND BY BURRELL AND ROBERTSON.

Temp. ° C.	Pressure, Mm. Hg.		Temp. ° C.	Pressure, Mm. Hg.	
	Brill.	Burrell and Robertson.		Brill.	Burrell and Robertson.
-80.0	35.2	37	-59.5	172.4	166
-79.0	38.0	45	-56.5	210.0	209
-77.6	44.1	45	-54.4	239.5	239
-75.1	51.8	53	-50.7	309.3	305
-72.7	62.5	65	-46.2	403.5	400
-70.4	74.9	76	-45.0	437.1	430
-68.3	87.5	88	-41.5	521.9	526
-64.4	116.0	117	-39.8	568.2	580
-62.8	136.0	132	-38.2	610.4	630
-60.8	157.6	151	-33.0	761.0	...

Brill's pressure measurements were performed by the statical method. His temperatures were measured with an iron-constantan thermocouple checked against a pentane thermometer calibrated at the physical-technical institute. The agreement between his work and that of the authors is fairly good, except at temperatures near the normal boiling point. His

¹ "Vapor Pressures of Liquid Ammonia," *Ann. Physik*, 21, 170 (1906).

value, 33.0° C., is 1.6° higher than ours. The authors of this report do not see one possible error in his work. As a check on the accuracy of his temperature measurements he calibrated his apparatus against the melting point of pure chloroform, assuming this to be 63.1°. Recent measurements by Henning, place it at 63.7°.¹

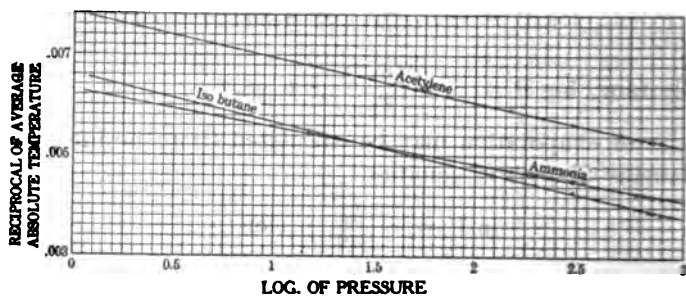


Fig. 2.—Log. of pressure plotted against reciprocal of absolute temperature.

Brill's work on ammonia is the only work on vapor pressures of gases at low temperatures that covers an extensive range for a gas that the authors also have worked on. We extended the observations 20° lower than Brill.

PITTSBURGH, PA.

[FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS COLLEGE.]

THE ACTION OF THIONYL CHLORIDE ON SULFIDES.

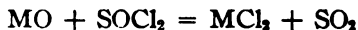
BY H. B. NORTH AND C. B. CONOVER.

Received September 1, 1915.

Investigation of the action of thionyl chloride on inorganic substances has been confined almost entirely to its deportment toward metals, metalloids and oxides. The action of the reagent on these has been quite exhaustively studied by North and Hageman and described in *THIS JOURNAL*.² Letting M represent a divalent metal or metalloid, reaction follows the general equation



With oxides, reaction takes place according to the following:



In the case of metals or metalloids having more than one compound with chlorine, the lower chloride is usually, but not always, produced if the metal is in excess. Likewise the higher chloride is formed when the metal is treated with a large excess of the reagent.

The chief difference in the two reactions given above is that with metals

¹ *Ann. Physik*, 43, 294 (1913).

² *THIS JOURNAL*, 34, 890 (1912); 35, 352 (1913); 35, 543 (1913).

or metalloids sulfur monochloride is always one of the products. Sulfur monochloride is not produced in reactions with oxides. In the case of higher oxides or peroxides, reaction does not follow the general equation given above but always results in the formation of a mixture of chloride, sulfate and sulfuryl chloride, if an excess of the oxide is used, or chloride, sulfur dioxide and sulfuryl chloride when an excess of thionyl chloride is employed.

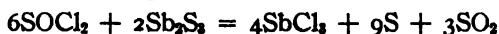
So far as the authors have been able to ascertain, only three reactions of thionyl chloride on sulfides have heretofore been studied. The action on phosphorus pentasulfide was studied in 1858 by Carius,¹ who undoubtedly was the first to prepare thionyl chloride in a pure condition. Carius thought the reaction proceeded according to the equation



but in 1884 Prinz² found this to be incorrect. According to Prinz the reaction takes place as follows:



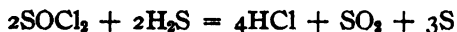
Prinz also tried the action of thionyl chloride on antimony trisulfide, finding that reaction takes place as follows:



Both of these reactions must have been carried out at a temperature lower than 150°, for above this point thionyl chloride and sulfur react according to the equation:



No further reaction with a sulfide was studied until 1896, when Besson³ investigated the reaction of this reagent on hydrogen sulfide. He found the reaction to proceed according to the following equation:



The reactions described in this paper were brought about in sealed glass tubes at a temperature of 150–180°. With the exception of ferrous sulfide, the sulfides employed were made by precipitation. They were thoroughly dried at 110° and were preserved in tightly stoppered tubes. In every case sulfur dioxide and sulfur monochloride were formed.

Zinc Sulfide.—When zinc sulfide was treated with thionyl chloride, reaction commenced in the cold but soon stopped. The sealed tubes containing the material were heated at 150–200° for several days without any change in appearance, due to the fact that both the chloride and sulfide are white. When the tubes were opened they were found to contain, in addition to the white solid, considerable sulfur dioxide and sulfur

¹ *Ann.*, 106, 303 (1858).

² *Ibid.*, 223, 355 (1884).

³ *Compt. rend.*, 122, 467 (1896).

monochloride. The white solid was analyzed and found to be zinc chloride. Reaction proceeds, therefore, according to the equation:

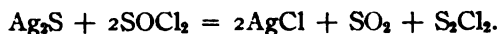


Cadmium Sulfide.—Reaction did not commence in the cold when cadmium sulfide and thionyl chloride were brought together. When the tube was heated at about 200° reaction appeared to take place slowly, as indicated by the very gradual change in color from yellow to white. After being heated for about 15 days, the solid contents of the tube appeared entirely white. Analysis showed this compound to be cadmium chloride, hence reaction proceeds as follows:



The tube also contained much sulfur dioxide and sulfur monochloride.

Silver Sulfide.—Thionyl chloride did not react with silver sulfide in the cold. After heating for several days the sulfide was found to have changed into silver chloride, as was shown by subsequent analysis. The action of thionyl chloride on silver sulfide proceeds according to the equation



Arsenic Sulfide.—Arsenic sulfide was found to react readily with thionyl chloride at 150° , going completely into solution. Inasmuch as thionyl chloride and arsenic chloride are both liquids and miscible, it was supposed that reaction had taken place with the formation of the latter compound according to the equation



The liquid in the tube was therefore a mixture of arsenic trichloride, sulfur monochloride and the excess of the thionyl chloride. This liquid was fractionated in an attempt to bring about a separation, but on account of the small amount of material, a complete separation was impossible. A small amount of distillate was obtained at a temperature above 126° . This had a very pronounced odor of sulfur monochloride, and when decomposed in water gave a precipitate of sulfur. The solution gave a strong test for arsenic, hence the authors are of the opinion that reaction took place according to the equation given and that the distillate obtained above 126° was a mixture of arsenic trichloride and sulfur monochloride.

Antimony Sulfide.—Antimony sulfide reacts readily with thionyl chloride at a temperature of 150 – 200° , giving the trichloride, sulfur dioxide and sulfur monochloride according to the equation



This reaction was studied by Prinz in 1884 and was found by him to result in the formation of a mixture of trichloride, sulfur monochloride

and sulfur. Prinz must have carried out this experiment below 150° or without excess of thionyl chloride, inasmuch as the latter reacts with sulfur at 150° to give sulfur dioxide and sulfur monochloride.

Ferrous Sulfide.—The sample of ferrous sulfide employed was the crude article such as is used for the preparation of hydrogen sulfide. An analysis of the powdered sample for iron and sulfur showed a slight excess of the latter. This would not interfere with the reaction, however, inasmuch as sulfur itself reacts with thionyl chloride, giving sulfur dioxide and sulfur monochloride.

The iron sulfide and thionyl chloride were heated together at 150° . Reaction took place readily with the formation of bright green, hexagonal plates which, by transmitted light, were ruby red. Analysis proved these to be ferric chloride, FeCl_3 . Reaction took place according to the equation



A small amount of light colored insoluble matter, probably silica, was obtained when the sample was dissolved in water for analysis. This was collected on a Gooch crucible, dried and weighed and the weight deducted from the weight of the sample.

This reaction differs from the others studied, inasmuch as the ferrous sulfide was oxidized to the ferric state. No indication of ferrous chloride was found.

Copper Sulfide.—Upon heating copper sulfide with the reagent at 150° , reaction took place within a few hours with the formation of a dark brown solid substance. This was analyzed and found to be anhydrous copper chloride. Reaction therefore took place according to the equation



Stannic Sulfide.—The material used for this experiment was the ordinary mosaic gold, made in the dry way. After heating for six hours at 150° no apparent change had taken place. The tube was then heated for a number of days at a temperature of from 150 to 200° , after which it was noticed that a considerable portion of the sulfide had dissolved. When the tube was opened sulfur dioxide was evolved. Furthermore, the odor of sulfur monochloride was very prominent. Considering this, together with the fact that the compound used was a compound of tetravalent tin, the authors are of the opinion that reaction proceeds slowly with the formation of tin tetrachloride according to the equation



The liquid in the tube was probably a mixture of tin tetrachloride, sulfur monochloride and the excess of thionyl chloride. An attempt was made to fractionate this, but it was a failure, due to the small amount of material at hand.

Mercuric Sulfide.—Mercuric sulfide was found to react readily with thionyl chloride at 150° with the formation of long needle crystals of mercuric chloride. Reaction proceeds according to the equation



Summary.

Thionyl chloride reacts with sulfides according to the following equation, in which M represents a divalent metal:



With sulfides as with oxides and metals, thionyl chloride seems to show a selective action, reacting much more readily with some than with others.

NEW BRUNSWICK, N. J.

THE DETERMINATION OF GASES DISSOLVED IN WATERS AND EFFLUENTS.

By A. A. SWANSON AND G. A. HULETT.

Received September 9, 1915.

The importance of a knowledge of gases dissolved in natural waters and effluents has led to the development of many methods for their estimation. The results obtained by these different methods are, however, not always concordant or satisfactory. Our attention was directed to this subject by some special difficulties encountered in the determination of the oxygen in mine waters and we were led to examine this whole subject of the determination of gases dissolved in waters and solutions. The method we have devised for our special purpose makes use of a principle which does not appear to have been used in this kind of work heretofore, but it has solved our problem and seems to be generally applicable.

The methods which have been used for the determination of gases dissolved in waters fall into two groups: First, those methods which are based on chemical reaction involving the gas in solution in a reaction which may be followed "titrimetrically." In the second group the gases are first removed from the water and then determined gasometrically. The chemical methods work well in the determination of oxygen and carbon dioxide, while no success has been attained in determining other dissolved gases such as nitrogen, owing to a lack of suitable chemical reactions.

At the present time most attention is given to the determination of oxygen and carbon dioxide in natural waters and effluents. The methods in favor for the determination of dissolved oxygen are the Winkler¹ and Levy² methods. A modification of the Winkler method by Hale and Melia³ has made it possible, however, to determine the dissolved

¹ *Ber.*, 21, 2843 (1888); 22, 1764 (1889).

² *Ann. l'obseratoire Municipal de Montsouris, Paris*, 1884.

³ *J. Ind. Eng. Chem.*, 5, 976 (1913).

oxygen content of waters containing nitrites. In the second group of methods the gases are first removed from the water either by boiling or under reduced pressure and then their composition determined gasometrically. In this class belong the methods devised by Bunsen,¹ Roscoe and Lunt,² Birge and Juday³ and Tenax.⁴ The accuracy of some of these methods is not questioned, but their adaptability for general use is limited on account of the difficulty encountered in removing the last traces of the dissolved gases and in handling the gases removed, but it seemed to be the only method in certain cases, especially where the chemical method is limited by the nature of the water under investigation. For example, in attempting to determine the dissolved oxygen in mine waters the presence of both ferrous and ferric iron interferes with the usual procedure, or, in general, where the water contains an oxidizable or a reducible substance. But this objection does not apply to the methods of the second group, although here there is encountered the difficulty of removing the last traces of the gases, as has been stated, and the methods have therefore received little attention.

If, now, we take advantage of the law of distribution of a gas between the liquid and vapor phase it will not be necessary to remove any, or at least all, of the gases dissolved in the water or solution in order to determine its amount. The ideal method of determining the amount of the gases dissolved in a water or solution would be to prepare and know the composition of a gas phase which was in equilibrium with our water at a known temperature and we could then calculate with accuracy from known data each constituent in the water. While we have not found a method of doing this, it has been found possible to bring the water into a vacuum, and, by shaking, to bring the system to equilibrium; so that the dissolved gases are properly distributed between the gas and liquid phase, then on analyzing the gas phase and knowing the temperature and volumes we calculate with accuracy from known coefficients of distribution⁵ the amounts of gases in the two phases, and have the desired information.⁶

¹ *J. Chem. Soc.*, 55, 552 (1889).

² *Ibid.*, 55, 552 (1889).

³ *Wisc. Survey Bull.*, 23 (1911).

⁴ *Plöner Forschungs ber.*, 11, 82 (1904); *Z. angew. Chem.*, 20, 1930 (1907); *Süßwasser*, 128 (1907).

⁵ *Landolt-Börnstein, Wied. Ann.*, 44, 318 (1891).

⁶ Dr. J. J. Johnson has just called our attention to an article by Fresenius and Gruenhut (*Z. anal. Chem.*, 53, 265). These authors worked with a "Schuettlerrohr" which was devised by E. Reichardt for determining CO₂ in mineral waters. The tube was partly filled with the water, closed and shaken, part of the CO₂ entered the gas phase increased the pressure and was allowed to displace an equal volume of the water. The tube gave a rapid method for an approximate determination of the CO₂ and was based on Henry's Law.

The apparatus we used to carry out this idea consisted essentially of two glass reservoirs or bulbs, cylindrical in form and having a capacity of one liter, and one-half liter, respectively. They were fitted with "120 degree" three-way cocks at the upper ends and with straight cocks at the lower ends. A short-range thermometer was fastened to the inner wall of the larger bulb so that it was possible to determine the temperature of the contents with certainty to 0.1° . These bulbs were mounted on a frame as shown in Fig. 1.

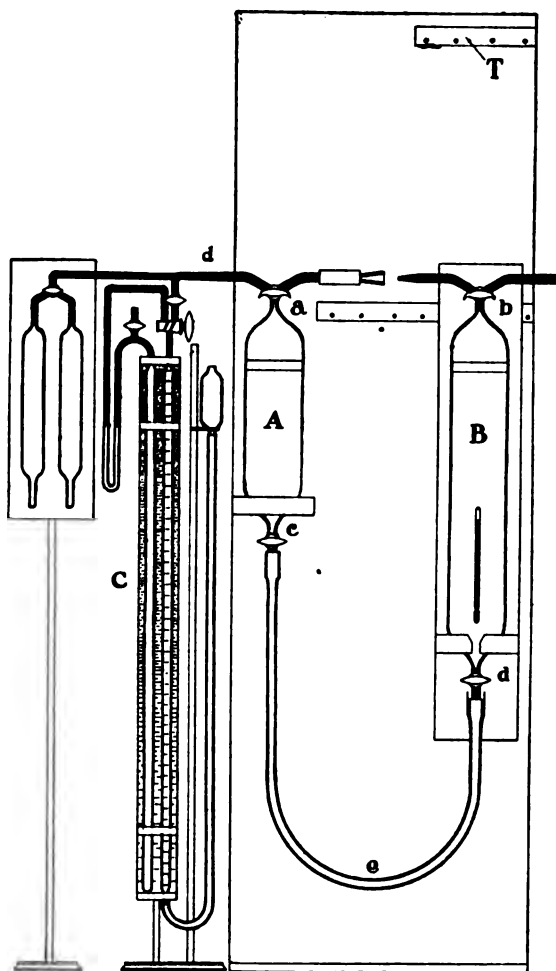


Fig. 1.

The small bulb A was permanently mounted while the larger bulb B was so arranged that its carriage permitted of either a horizontal motion or of being raised vertically. Bulb A was connected with a gas analysis apparatus of special design, C, through a capillary tube, d. The two bulbs were made and mounted so that they could be joined at either end with each other at will.

The water to be examined was drawn directly into bulb B and the cocks closed and there could then be no gain or loss of gases. In making a run bulb B, with the water under examination, was placed on its carriage

and then joined to the lower end of bulb A, by means of suitable tubing and a mercury seal so that there was no air in the connections. On opening the lower cocks on bulbs A and B, the mercury in A flowed by gravity into the lower half of bulb B and displaced an equal volume of water through the upper cock on bulb B. This water was reserved for any

special tests. Cock *b* was closed and the carriage with the bulb B raised to the position indicated at T and the mercury allowed to flow back to bulb A, leaving the water in bulb B in a vacuum; the lower cock on bulb B was then closed and the bulb was removed from its support and shaken vigorously in order to bring the liquid and vapor phases into equilibrium. This operation required only a couple of minutes. The bulb B was then replaced on the carriage and lowered to its original position and again connected with the lower end of bulb A. The carriage was then moved along the slide rail so that bulbs A and B were joined at the upper ends by means of a ground-glass joint. Cocks *a* and *b* were then made communicating and the line evacuated and mercury allowed to fill the line to the cock *b*. The system was then ready for a transfer of the gas from bulb B to bulb A without changing its pressure, an equal volume of mercury flowing from bulb A to bulb B. Then the gas could safely be brought to any desired pressure over mercury, transferred to the gas buret, and analyzed in the usual way. It was not desirable to change the pressure of the gas while in contact with the water, as some of it would dissolve.

From the amount of the gases found, the volume and temperature when in equilibrium with the water in bulb B, and the known coefficients of distribution of the gases, the total amounts of the gases dissolved in the water was calculated. The following formulas were used to calculate the amount of dissolved gases in the waters examined:

$$x = a \left(\frac{c(T + t)}{T} + 1 \right)$$

Where *x* = total number of cc. of the particular gas in the sample of water taken for analysis.

a = number of cc. of the desired gas actually removed.

c = solubility coefficient of the gas at the temperature observed.

t = temperature at which the gas and liquid phases were at equilibrium.

T = absolute temperature of Centigrade scale.

In case the volume of the liquid and gas phases in the bulb were not equal the above equation was modified as follows:

$$x = \frac{a}{b} \left(\frac{bc(T + t)}{T} + d \right)$$

Where *b* = volume of the liquid phase.

d = volume of the vapor phase.

The accompanying Tables (I), (II), (III) of several series of determinations show the agreement we obtained by the use of this method in determining dissolved oxygen in various waters. The results thus found were calculated to standard conditions of temperature and pressure and are expressed in cubic centimeters of oxygen gas per liter of water

as is customary. The method was first tested by running check determinations against the "Winkler" method.¹ Distilled water thoroughly aerated was used for part of the tests, so there was nothing present which could be oxidized and nothing reduced save the oxygen, so the Winkler method should give correct values.

TABLE I.—TO SHOW AGREEMENT WITH THE WINKLER METHOD.

Amt. of oxygen removed.	Equil. temp.	Temp. of analysis of gas.	Bar pres. in mm.	New meth. Cc. per liter.	Winkler.
3.18 cc.	21.4°	21.3°	759.20	6.22	6.22
3.19	21.3	21.0	766.30	6.26	6.26
3.19	22.7	22.3	755.75	6.16	6.14
3.16	22.7	22.3	756.60	6.11	6.13
3.26	20.9	20.3	762.00	6.41	6.41
3.34	19.4	19.1	766.75	6.65	6.63
3.33	22.8	22.4	762.35	6.48	6.52
3.21	23.2	23.4	762.80	6.22	6.27
3.07	21.2	23.6	745.40	5.86	5.84
3.04	22.0	23.0	753.70	5.83	5.86
4.68	18.1	19.88	749.70	9.06	9.07

TABLE II.—TO SHOW THE REPRODUCIBILITY OF OUR METHOD.
Distilled Water.

3.00 cc.	23.0°	23.5°	749.90	5.708	5.707
3.02	23.4	24.0	748.85	5.730	
3.01	22.9	23.8	749.25	5.717	
3.00	22.6	23.5	749.25	5.703	
2.98	22.5	22.4	750.15	5.705	
3.00	23.0	23.0	750.15	5.724	

TABLE III.—TO SHOW AGREEMENT ON VARIOUS WATERS.

Amt. of oxygen removed.	Equil. temp.	Temp. of analysis of gas.	Bar pres. in mm.	New method.	Winkler method.
3.94 cc.	22.3°	24.0°	761.80	7.60	7.62 ¹
3.94	21.6	23.5	761.80	7.62	
3.93	22.2	23.3	760.10	7.59	
4.33	20.1	20.0	756.65	8.47	8.51 ¹
4.35	17.2	20.0	756.55	8.52	
3.88	22.0	23.5	760.10	7.49	7.55 ¹
3.90	22.0	23.7	759.65	7.51	
3.45	22.8	23.0	755.70	6.63	6.59 ¹
3.46	22.9	23.2	755.70	6.64	
3.63	21.7	22.0	765.25	7.20	7.09 ¹
3.60	21.5	22.0	765.25	7.05	
4.42	17.4	20.0	767.75	8.79	9.62 ⁴
4.43	17.2	20.0	767.75	8.81	

¹ *Wied. Ann.*, 44, 318 (1891).² Water from city tap.³ Water from pond.⁴ Water from sewage effluent.

Carbon Dioxide.

Of the several methods which have been proposed for the determination of free carbon dioxide in water, the so-called Seyler's modification of the Pettenkofer¹ method seems to be the one most easily adapted and the most reliable one. It has been fully described by Seyler in the *Chemical News*² and recently has received exhaustive study of Ellms and Beneker,³ who reached the conclusion that it gives the most accurate results. It consists of titrating with sodium carbonate and phenolphthalein. As soon as the free acid is neutralized any further addition of sodium carbonate produces a pink color. In using distilled water where there are no complications due to the equilibrium of the dissolved carbonates and the free carbon dioxide in solution, the method should give reliable results.

We have applied our method to the determination of free carbon dioxide in distilled water and have found it to be in excellent agreement with the Seyler method. The same general procedure was carried out in determining the carbon dioxide, as was used for the determination of dissolved oxygen. The same formula as was used in calculating the amount of dissolved oxygen is applicable and was made use of in the following determinations. (See Table IV.)

TABLE IV.—TO SHOW AGREEMENT WITH THE SEYLER METHOD.

Amt. of gas removed.	Equil. temp.	Anal. temp.	Bar pres.	New meth. Cc. CO ₂ per l.	Seyler meth.
0.45 cc.	20.1°	20.0°	749.49	1.74	1.81
0.46	19.6	20.0	749.49	1.77	1.80
0.46	21.4	20.5	749.49	1.70	1.81
0.14	25.0	20.0	753.60	0.51	0.51
0.14	24.7	20.0	753.60	0.51	0.51
0.14	24.8	20.0	753.60	0.50	0.51

TABLE V.—TO SHOW THE REPRODUCIBILITY OF OUR METHOD.

0.53	21.7	23.3	764.80	2.01	2.00
0.52	21.0	23.1	764.80	1.99	2.00
0.52	21.4	23.5	765.20	1.98	2.00
0.52	21.2	23.0	764.80	2.02	2.00
0.53	22.2	23.3	760.10	1.98	2.00

Nitrogen.

From a survey of the literature it was found that a little work has been done on the determination of dissolved nitrogen in water. There seems to be no valid reason why a knowledge of the amount of the dissolved nitrogen would not find an important place in the analysis of waters and effluents were it possible to determine it readily.

We were particularly interested when designing our method to make

¹ *N. Rep. Pharm.*, 19, 1.

² *Chem. News*, 70, 104.

³ *THIS JOURNAL*, 23, 405 (1901).

it general in application and thereby the determination of dissolved nitrogen of no less importance than that of dissolved oxygen and carbon dioxide now so widely used for the studies of pollution in harbors and river waters in this country and in England.

The only attempt to determine the dissolved nitrogen in water has been along the lines of completely removing the dissolved nitrogen by boiling out the gas under reduced pressure. One has, however, but to turn to the work of Roscoe and Lunt¹ or Birge and Juday² on the determination of dissolved nitrogen to learn of the experimental difficulties encountered by this general method.

By the application of our method we have determined the dissolved nitrogen in water very readily. We have checked the results obtained experimentally by the calculation of the theoretical amount thoroughly aerated water can hold at the particular temperature and pressure. We found that the calculated value was in excellent agreement with the amount determined by experiment.

In the following tables are given the results obtained from a set of duplicate determinations using distilled water:

TABLE VI.

Amt. of gas removed.	Equil. temp.	Anal. temp.	Bar. pres.	New method. Cc. nitrogen per liter.
8.06 cc.	22.2°	24.0°	761.80 mm.	15.28 cc.
8.06	21.6	23.5	761.80	15.31
8.06	22.2	23.3	760.10	15.33
8.08	21.7	23.3	764.80	15.46
8.08	21.0	23.1	764.80	15.45
8.07	21.2	23.0	764.80	15.44

TABLE VII.

6.52	23.0	23.5	728.40	12.18
6.54	23.4	24.0	726.80	12.17
6.53	23.4	24.2	726.83	12.16
6.52	22.6	23.5	727.75	12.17
6.51	22.9	23.8	727.36	12.14
6.50	23.0	23.0	729.29	12.15

Another Apparatus for the Determination of Dissolved Oxygen

The principle of the method already described by us for the determination of dissolved gases in water depends upon the establishment of an equilibrium between the gas in the gas phase and that in solution. This was accomplished by bringing the water into a vacuum and shaking until equilibrium was established. We could, however, just as well have used an indifferent gas as a vacuum and by shaking it with the water under examination established an equilibrium between the two phases. When the equilibrium is established the gas phase can be removed

¹ *J. Chem. Soc.*, 55, 552 (1889).

² *Wisc. Survey Bull.*, 23 (1911).

analyzed for the gas under consideration. The total amount of the gas dissolved in the water may be calculated by the aid of the formula previously mentioned.

In the determination of dissolved oxygen by this scheme hydrogen was first used as the indifferent gas in which the equilibrium was established. A glass bulb of a liter capacity was filled with the water under consideration. Hydrogen was then allowed to displace half of the water, after which the equilibrium was established by vigorous shaking of the bulb containing the water and the indifferent gas. The gas phase was then removed and measured in a specially designed buret. A platinum wire within the buret was then brought to a bright glow by an electric current, whereby the hydrogen and oxygen in the mixture of gases were caused to combine to form water, *i. e.*, $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$, which condensed upon the walls of the buret. We have here the advantage of a contraction of three volumes for each volume of oxygen, but we have here also the disadvantage due to the fact that the volume of the oxygen was only 1 to 2% of the total gas volume. If the total volume was 100 cc., then the volume measurements should be reliable to 0.01 cc or less, in order to secure an accuracy of 0.1% of the oxygen. This means a more accurate control of the temperature and pressure before and after burning out the oxygen than can conveniently be secured in routine work, therefore, we sought other ways of determining this oxygen.

Oxygen may be readily removed from a mixture with an indifferent gas by copper, so we brought our sample of water into a nitrogen atmosphere and established equilibrium. The gas phase was then passed through potassium hydroxide solution to remove carbon dioxide, then over glowing copper, which picks up the oxygen. The amount of oxygen uniting with the copper was then determined indirectly by reheating the copper glower in the presence of hydrogen; the amount of hydrogen necessary to effect complete reduction to metallic copper being measured, the amount of oxygen being one-half of this amount. By this means we were able to obtain measurements on a relatively small volume of hydrogen and consequently we could readily obtain the desired accuracy. If, however, CH_4 or organic vapor of any kind gets into the gas phase they would be oxidized by the CuO and O_2 and so too little O_2 found. This difficulty could be overcome, as the N_2 which passed would contain the CO_2 formed from the combustion of CH_4 and it could be determined, but in our work we have had no evidence of the presence of oxidizable gases or vapors in the gas phase. The apparatus we used to carry out this idea is shown in Fig. 2.

The apparatus consists of a glower, A, made by winding nichrome resistance ribbon spirally upon a quartz tube 28 cm. in length and 3 mm. internal diameter, 5 mm. external diameter. Fourteen centimeters of the tube

were heated by the resistance ribbon, within which region strips of pure copper foil one-thousandth of an inch thick were placed in such a manner as to permit of maximum surface exposed. The use of copper of extreme thinness was found necessary, owing to the difficulty encountered when using thick copper of a slow rate of reduction of the copper oxides by hydrogen, the final value being obtained only after several heatings. This effect was probably due to the formation of cuprous oxide, which penetrated beneath the surface of the copper. By the use of the very thin copper foil this slow rate of reduction was obviated and one heating of the glower to $550-600^{\circ}\text{C}$. from 3 to 4 minutes was sufficient. The ends of the quartz

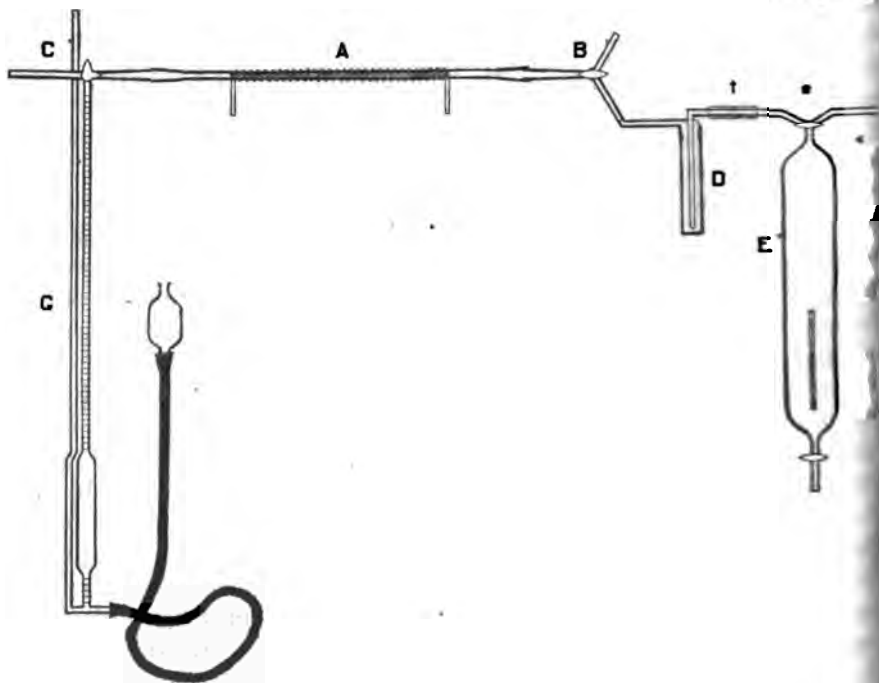


Fig. 2.

tubes were flared to meet a glass complement which was ground to fit. To make these joints perfectly secure a thin coating of hard Khotinsky cement was applied and the two parts fitted together while hot. At either end of the short glass capillaries joined to the quartz tube were sealed three-way stopcocks, *viz.*, B and C, Fig. 2. One of the arms of the cock B was connected to a hydrogen generator by means of a glass tube in which was placed a small platinum glower. The glower served to free the hydrogen gas from any possible oxygen or organic matter that it might contain. The other arm of cock B was joined to a wash bottle, D, of special design, through which the gases, as they came from bulb E, were

bubbled to remove carbon dioxide. To one of the arms of the 3-way cock C at the other end of the quartz tube there was connected a calibrated gas buret, G, graduated to read to hundredths of cubic centimeters. To this buret was fitted a mercury leveling bulb and a manometer to aid in obtain accurate readings. The other arm of the cock C was connected to the air through a small wash bottle.

The water to be examined was drawn directly into a glass bulb, E, of a liter capacity. It was fitted with a 3-way cock on either end and carried a short range thermometer within graduated to read to tenths of degrees. This bulb was arranged on a carriage so that it could be easily removed in order to shake the contents. After the bulb E was filled with the water it was connected to a source of oxygen-free nitrogen by one of the arms of the upper cock; water was then drawn from the bulb by opening the lower cock until half of the water in the bulb was displaced by the nitrogen gas. The cocks were then closed, the bulb E removed from the carriage and shaken vigorously for five minutes, after which time the gas in the gas phase and the gas in solution were in equilibrium. The bulb was then replaced upon the support and connected to the glower by means of a ground-glass joint. The gas above the water was then displaced without changing the pressure by permitting water to enter the bulb E through the lower cock, from a reservoir kept at a temperature corresponding to the temperature within the bulb. The gas displaced from the bulb was bubbled through caustic potash solution in the washer B and thence into the quartz glower where the oxygen was picked up by the glowing copper. When the gas had all been displaced from bulb E the cock *e* was turned to permit the system to be swept out by nitrogen in order to carry through the glower any oxygen in the wash bottle or connections. The glower was then allowed to cool in a nitrogen atmosphere. When it had reached room temperature hydrogen gas was passed through the glower and after the system had been thoroughly swept out by the hydrogen, the cock C was turned to permit the gas buret G to become filled, then cock B was closed and the current again turned onto the glower. The copper which was in part oxidized in the passage of the oxygen laden nitrogen from the bulb E was now reduced by the hydrogen entering the glower from the buret as fast as it was used up in reduction. The water formed from the union of the hydrogen and oxygen condensed upon the cold walls of the glower. After complete reduction the glower was allowed to cool to room temperature when the difference in the readings of the mercury in the buret gave the amount of hydrogen which had been used to effect reduction, account being taken of the volume occupied by the condensed water and change in volume of CuO going to Cu. The amount of hydrogen in the buret before reduction was usually 8 cc., after reduction 0.5 to 1.0 cc. remained in buret. The

amount of oxygen actually removed from the sample of water was equal to one-half of the hydrogen volume used up in the reduction as the combining volume; ratios of oxygen to hydrogen is as 1 : 2. From the amount of oxygen thus determined a knowledge of the actual amount of dissolved oxygen in the sample of water was obtained by use of the formula given in the first part of this paper.

It was evident when making a run that all of the oxygen was being picked up, as a considerable portion of the glowing copper opposite the end at which the gas mixture entered remained bright, showing no trace of oxidation.

In the following table are given the results obtained by the use of this method in determining the amount of dissolved oxygen in distilled water. Both the Winkler¹ and our first method for determining oxygen were run as checks on the above method.

TABLE VIII.

Amt. of oxygen removed.	Equil. temp.	Room temp.	Bar. pressure.	New meth. Cc. per liter.	Winkler meth.
3.22 cc.	21.0	20.8	755.00	6.42	6.40
3.25	20.5	21.0	755.00	6.48	6.40
3.26	21.8	20.5	755.00	6.49	6.46
3.22 21.8	21.8	20.5	755.00	6.43	6.45
3.25	21.8	20.5	755.00	6.47	6.44
3.20	21.5	20.0	755.02	6.39	6.40
3.22	21.7	20.1	755.02	6.42	6.40
3.20	21.6	20.0	755.02	6.40	6.40
3.22	21.5	20.2	755.02	6.42	6.40
3.24	21.7	20.0	754.00	6.47	6.40
3.20	21.4	20.1	754.00	6.39	6.40

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

OBSERVATIONS UPON THE QUANTITATIVE DETERMINATION OF FLUORINE.

BY WILLIAM H. ADOLPH.

Received September 4, 1915.

Berzelius² originally precipitated and weighed fluorine as calcium fluoride. Rose³ suggested the precipitation of the fluoride in the presence of carbonate to facilitate filtering. The ignition of this combined precipitate and its subsequent extraction with acetic acid left calcium fluoride in a granular form which was easily filtered. The extraction has usually been made with 1.5 *N* acetic acid. To test the solubility of calcium

¹ *Ber.*, 21, 2843 (1888).

² *Schweigg. Jour.*, 16, 426 (1816).

³ *Leib. Ann.*, 72, 343 (1849).

fluoride in acetic acid of this strength, weighed amounts of perfectly pure material were digested in 10 cc. of the acid on the water bath for an hour, filtered, washed and weighed. The mean loss for 10 cc. of the acid equaled 0.0015 g. calcium fluoride.

A portion of the same calcium fluoride, after treatment with acetic acid, was exposed for one hour to a red heat over an ordinary Bunsen flame, when 0.0886 g. of material lost 0.0016 g. The change upon ignition was probably due to the formation of calcium oxide with the evolution of hydrogen fluoride.

It was found by repeated experiments that, if the substance which had been ignited with consequent loss of weight was covered with hydrofluoric acid, evaporated to dryness and weighed, the original weight was restored. Thorium and cerium fluorides, upon ignition, pass into the corresponding dioxides.

To a solution of sodium fluoride, there was added a small amount of sodium carbonate, the precipitate produced in this solution, by calcium chloride, was filtered, ignited and treated with 10 cc. of 1.5 *N* acetic acid. The acid was evaporated to dryness, the residue taken up in hot water, filtered and weighed. This was done with several samples.

F. present.....	0.0344 g.	0.0344 g.	0.0344 g.	0.0688 g.	0.1423 g.
F. found.....	0.0329 g.	0.0330 g.	0.0328 g.	0.0664 g.	0.1401 g.
Loss.....	0.0015 g.	0.0014 g.	0.0016 g.	0.0024 g.	0.0022 g.

The error here is not proportional to the amount of fluorine present, but is an additive one depending upon the solubility of calcium fluoride in a given quantity of acetic acid. Consequently the method which has been suggested may be successfully employed by applying a constant correction factor.

To test the delicacy of the calcium fluoride precipitation, quantities of sodium fluoride were dissolved in 50 cc. of water, warmed and treated with a solution of calcium chloride.

NaF present.	F present.	CaF ₂ found.	F found.
0.0003 g.	0.0001 g.	No precipitate
0.0009	0.0004	No precipitate
0.0015	0.0006	No precipitate
0.0022	0.0009	Slight turbidity	...
0.0037	0.0016	Distinct turbidity
0.0066	0.0028	0.0047	0.0023 g.

It has been long known that simple fusion of fluor spar or calcium fluoride with sodium carbonate will not convert all of the fluorine into a soluble form. The addition of silica to the fusion mixture does, however, bring this about. So, in applying the method of Berzelius to insoluble fluorides and minerals, it has been customary to mix the fluor spar, let us say, with four times its weight of silica and six times its weight of a

Bein¹ led the gas into water and estimated the separated silica. Lasne² adopted the laborious method of precipitation of the fluorine from this solution as calcium fluoride after first separating the silica.

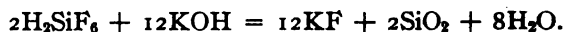
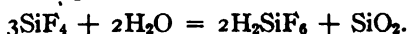
Tammann³ precipitated the hydrofluosilicic acid formed as potassium silicofluoride in alcoholic solution, filtered and titrated the precipitate with standard caustic potash, while Carnot⁴ precipitated K_2SiF_6 by the reaction



The handling of the gelatinous precipitate of potassium silicofluoride is not a simple matter; it has been shown to be not completely insoluble even in 50% alcohol. The Carnot method has invariably given lower results than the other procedures.

The alkalimetric methods are the most rapid and by far the most convenient. Penfield⁵ received the silicon tetrafluoride in an alcoholic solution of potassium chloride, and titrated the hydrochloric acid set free, using cochineal as indicator.

Offermann⁶ received the gas in water and, using phenolphthalein, titrated according to this equation



Both of these methods are rapid and in the past have given good results. The method of Offermann⁶ is to be preferred.

My experiments were concerned more with the circumstances surrounding the evolution of the silicon tetrafluoride.

The apparatus involved nothing new, but was an attempt to assemble the best recommendations made in previous investigations. A and B contained concentrated sulfuric acid; C soda-lime and D, calcium chloride, these to dry the air current. F was made from a 100 cc. distilling bulb. The entrance tube into F formed a ground joint with the neck. F was heated by means of an air bath. G was a small flask containing concentrated sulfuric acid. H, I and J served to condense any sulfuric acid carried over. H contained glass beads. I and J were empty. H and I were surrounded by cold water. K was an 8-inch test tube containing the water into which the silicon tetrafluoride was received. It was found unnecessary to employ a layer of mercury in the bottom of K. The danger of the tube becoming clogged by deposited silica was obviated by spreading the end of the tube as indicated. Air pressure was furnished at A by a

¹ *Z. anal. Chem.*, 26, 733 (1887).

² *Bull. soc. chim.*, [2] 50, 167 (1887).

³ *Z. anal. Chem.*, 24, 328 (1885).

⁴ *Compt. rend.*, 114, 750, 1189 (1892).

⁵ *Am. Chem. J.*, 1, 27 (1879).

⁶ *Z. angew. Chem.*, 3, 615 (1890).

water pump. This was found more convenient than a gasometer and furnished a more constant stream of air than a suction pump at K. A number of preliminary experiments were made to ascertain the most suitable conditions of temperature, etc.; 0.1 g. samples of calcium fluoride

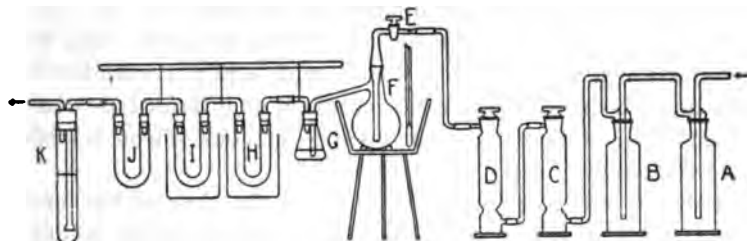


Fig. 1.

were mixed with 0.5 g. powdered quartz and placed in the decomposition flask F. A temperature of 180° was used in the preliminary experiments. These determinations were carried out in the main in accord with the detailed description of the method below.

Observations upon the Concentration of Sulfuric Acid Required.—Determinations employing laboratory acid labelled "concentrated" (analysis = 96.9% H_2SO_4).

CaF_2 present.	F found.	F found.	F theor.
0.1052 g.	0.0425 g.	40.4%	48.52%
0.1298	0.0570	43.9	...

Determinations employing acid prepared by heating the above acid in a retort till about one-tenth of the volume had passed over (method of Daniel) (analysis = 98.6% H_2SO_4). This corresponds to "constant boiling" acid.

CaF_2 present.	F found.	F found.	F theor.
0.0930 g.	0.0436 g.	46.9%	48.52%
0.1418	0.0678	47.8	...

Seemann has shown that an acid of higher percentage formed by the addition of sulfur trioxide gives off the trioxide on heating, and is difficult to condense.

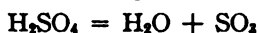
TABLE II.—VARIATIONS IN TEMPERATURE.

Temperature.	CaF_2 present.	F found.	F found.	F theor.
1..... 180°	0.0930 g.	0.0436 g.	46.9%	48.52%
2..... 180	0.1418	0.0678	47.8	...
3..... 200	0.1243	0.0589	47.4	...
4..... 220	0.1211	0.0570	47.1	...
5..... 230	0.1225	0.0583	47.6	...
6..... 280	0.1245	0.0564	45.3	...
7..... 310 (b. p.)	0.1100	0.0393	35.7	...
8..... 310 (b. p.)	0.1002	0.0327	32.6	...

The results shown in Table II would indicate a temperature of 200–220° as most desirable. In Experiments 4 and 5, after titrating the solution in K, the acid in the decomposition flask was raised to the boiling point for 15 minutes and the air current continued for 1 hour longer. It was hoped in this way to obtain any fluorine which might not be expelled at 220°, but which might be driven over by boiling the acid. The water in K still showed neutral reaction. This would seem to contradict Daniel¹ and Hileman,² who maintained the formation of an intermediate compound which was only completely broken up into gaseous silicon tetrafluoride on boiling the sulfuric acid.

Repeatedly in later determinations, toward the close of the operation, the temperature of the decomposition flask was raised to the boiling point of sulfuric acid, but no increase in the amount of silicon tetrafluoride evolved was indicated.

It was also noted that when heated over 280° the contents of the decomposition flask (which included always 1 g. of anhydrous copper sulfate) changed from white to a blue color, undoubtedly indicating that at this temperature even "constant boiling" sulfuric acid decomposes thus:



One of the most important conditions for the success of the method, where silicon tetrafluoride is evolved, has been the exclusion of every trace of moisture from the apparatus. However, it cannot be overlooked that water is one of the products of the reaction and is just as influential a factor as the concentration of the sulfuric acid used. The introduction of a dehydrating agent to take up this water is an obvious step. Drawe³ suggested the use of anhydrous copper sulfate. Quantitative measurements showed:

CaF ₂ present.	Quartz present.	Dehydrating agent.	Time. Hours.	F found.	F found.	F theor.
0.1019 g.	0.33 g.	None	3	0.0484 g.	47.5%	48.52%
0.1243	0.50	2 g. CuSO ₄	5	0.0589	47.4	...
0.1211	0.50	2 g. CuSO ₄	3 1/2	0.0570	47.1	...
0.0799	0.30	1 g. P ₂ O ₅	3 1/4	0.0380	47.5	...

The form of silica used in the formation of silicon tetrafluoride is another factor strangely affecting the reaction. Daniel found quartz preferable to precipitated silica and showed that it is more easily attacked by hydrofluoric acid than other varieties of silica. Drawe suggested the use of powdered feldspar as a "more easily combinable form" of silica. Measurements with varying quantities of each showed the results given in Table III.

¹ *Z. anorg. Chem.*, **38**, 257 (1904).

² *Am. Jour. Sci.*, [4] **22**, 329, 383 (1906).

³ *Z. angew. Chem.*, **25**, 1371 (1912).

TABLE III.
Quartz.

CaF ₂ present.	Gram added.	Time. Hours.	F found.	F found.	F theor.
0.1243 g.	0.50	5	0.0589 g.	47.4%	48.52%
0.1211	0.50	3 $\frac{1}{2}$	0.1570	47.1	...
0.1225	0.23	4	0.0583	47.6	...
0.0900	0.08	3 $\frac{1}{2}$	0.0413	45.9	...
Precipitated silica present.					
0.0859	0.20	8	0.0378	44.0	48.52
Feldspar present.					
0.1013	0.59	2 $\frac{3}{4}$	0.0466	46.0	48.52
0.1168	0.50	2 $\frac{1}{4}$	0.0540	46.3	...
0.0696	0.45	2 $\frac{1}{2}$	0.0325	46.7	...
0.0781	0.40	2 $\frac{1}{2}$	0.0361	46.2	...
0.0641	0.35	2	0.0293	45.7	...
0.1547	0.20	3 $\frac{1}{2}$	0.0719	46.4	...

The results in using quartz were the most satisfactory, while the application of silica in the form of feldspar evolved the gas in a manner which was more easily swept along to the absorption tube, with a consequently much shorter time required for the determination. When quartz was employed, a continued agitation of the decomposition flask was necessary to break up the small bubbles of gas remaining collected on the surface of the sulfuric acid, while with feldspar the silicon tetrafluoride was evolved on heating almost as readily as is carbon dioxide from a carbonate on treatment with acid.

The Details of the Offermann Method.—The standardized procedure which the above experiments seemed to recommend, and which was used in all the subsequent determinations follows: The sample of calcium fluoride weighing 0.1–0.2 g. was mixed in a mortar with three times its weight of powdered quartz. (The quartz had been strongly ignited and kept in a desiccator.) This was placed in F, about 1 g. of anhydrous copper sulfate was added and 25 cc. of concentrated sulfuric acid introduced. (The sulfuric acid was prepared by the method of Daniel.) With the stopcock at E closed, the air bath was heated gradually till in $\frac{1}{2}$ hour the temperature had risen to 220°. E was then opened to let an air current of about three bubbles per second pass through the apparatus and the temperature kept at 220°. Occasional shaking of the evolution flask was found desirable. When the bubbles of silicon tetrafluoride had disappeared from F, the flame was removed, the air current continued, and after about $\frac{1}{2}$ hour the solution in K was titrated with 0.1 N KOH. The entire determination for fluorspar required about 2 $\frac{1}{2}$ hours. A single vessel at K containing 50 cc. of water was found sufficient for the complete absorption of the evolved gas. Another tube attached after K gave always a blank test. The apparatus employed, at the specified

temperature, succeeded in completely condensing all sulfuric acid before reaching K. After twenty successive determinations, the apparatus was taken apart and the tubes H, I and J tested by washing out with a little water. That from H showed a distinct acid reaction with litmus, I was very slightly acid, while J showed a neutral reaction. A total of fifty determinations was made by this method.

As the addition of feldspar to the contents of the evolution flask showed an interesting behavior, observations were made upon other minerals. In each case the mineral was finely powdered and intimately mixed with the calcium fluoride before this was placed in the decomposition flask.

TABLE IV.

	Form of silica present.	CaF ₂ present.	Time. Hours.	F found.	F found.	F theor.
Calamine.....	0.59 g.	0.1153 g.	2 1/2	0.0522 g.	45.3%	48.52%
Calamine.....	0.41	0.0919	3	0.0418	45.5	...
Leucite.....	0.38	0.0824	4	0.0366	44.5	...
Powdered glass.....	0.135	0.1321	5	0.0612	46.3	...
Sodium silicate.....	0.37	0.0961	6	0.0219	22.8	...
Wollastonite.....	0.46	0.1138	2 1/4	0.0366	32.1	...
Wollastonite.....	0.56	0.1072	2 1/2	0.0317	29.6	...
Pyroxene.....	0.50	0.0691	2 1/2	0.0316	45.7	...

These measurements are interesting in showing the manner in which different forms of silica, or at least different forms of silicate combinations, may affect this reaction.

Since different forms of silica presented a varying behavior, it was sought to determine whether mineral fluor spar behaved in the same manner as precipitated calcium fluoride. The following results were obtained (Table V):

TABLE V.

Fluorspar present.				
Wt. taken.	Quartz.	F found.	F found.	F theor.
0.1256 g.	0.50 g.	0.0592 g.	47.2%	48.50%
0.1130	0.50	0.0537	47.5	...
0.0783	0.50	0.0371	47.3	...
CaF ₂ artificial.				
0.0243 g.	0.50 g.	0.0589 g.	47.4	48.52
0.1211	0.50	0.0570	47.1	...
0.1225	0.23	0.0583	47.6	...

Apparently there was no difference in the behavior of these two forms of calcium fluoride.

The fact that the best determinations by the Offermann method are low is still to be explained. The general belief has been that there is formed in the course of the reaction an oxyfluoride of silicon, perhaps of the formula SiOF₂, which is not decomposed by sulfuric acid. The varied behavior of the several silicates in the reaction as shown above is probably explained

by the formation of such a compound. The aim, therefore, should be to get conditions least favorable to the formation of this oxyfluoride. The solid residue remaining in the decomposition flask at the conclusion of each determination was repeatedly tested for fluorine, but the methods employed failed to detect it.

Starck¹ in estimating fluorine takes advantage of the double halide formed on adding lead chloride to a solution of soluble fluoride, PbFCl . It is unfortunately only applicable to soluble fluorides and to those in neutral solutions. Lead chlorofluoride is quite appreciably soluble in water, but insoluble in a saturated solution of lead chloride. A number of other soluble lead salts and other soluble chlorides were examined, but none found which would render the chlorofluoride insoluble to the same degree. The real difficulty of the method lies in the washing of the precipitate, which is a delicate matter even with the use of a Gooch crucible, and requires the very least amount of wash water. The precipitate is dried and weighed as such in a Gooch crucible. It was found desirable to wash with ice-cold water. Satisfactory results may be obtained under carefully standardized conditions. An obvious advantage of the method is the fact that the precipitate weighed is about fourteen times the weight of the fluorine it contains. A solution of sodium fluoride was employed and treated according to the original directions.

F present.....	0.0344 g.	0.0344 g.	0.0492 g.	0.0863 g.
PbFCl found.....	0.4757 g.	0.4738 g.	0.6743 g.	1.1941 g.
F found.....	0.0345 g.	0.0344 g.	0.0490 g.	0.0867 g.

These figures are typical of a larger number of analyses which confirm those reported by Starck.¹

An "alundum" filter cone was substituted for the Gooch crucible. The washing of the precipitate on the cone was found to require a greater amount of wash water and the results were correspondingly low. It was then thought possible to use in washing the precipitate, instead of pure water, a saturated solution of lead chlorofluoride itself. This was employed and gave more satisfactory results as follows:

F present....	0.0344 g.	0.0344 g.	0.0344 g.	0.0344 g.	0.0344 g.
PbFCl found	0.4641 g.	0.4712 g.	0.4744 g.	0.4816 g.	0.4773 g.
F found.....	0.0337 g.	0.0342 g.	0.0344 g.	0.0350 g.	0.0347 g.

Guyot² and Greeff³ have evolved a volumetric method based on the precipitation of the salt Na_3FeF_6 upon the addition of standard ferric chloride to a solution of a soluble fluoride. This precipitation is complete in the presence of alcohol and an excess of sodium chloride. The end point is read by the use of thiocyanate as indicator and absorption of the red

¹ *Z. anorg. Chem.*, **70**, 173 (1911).

² *Compt. rend.*, **71**, 274 (1870).

³ *Ber.*, **46**, 2511 (1913).

thiocyanate color in an ether layer. A standard solution of ferric chloride was used, of such value that 1 cc. = 0.00267 g. of fluorine. Bellucci¹ has shown the effect of varying the quantity of pure sodium chloride present. The method was applied to a solution of sodium fluoride according to the recommendations of Greeff, and gave reliable results.

F present.....	0.0344 g.	0.0344 g.	0.0993 g.	0.0585 g.
NaCl present.....	1 g.	1 g.	2 g.	1 g.
F found.....	0.0339 g.	0.0339 g.	0.0995 g.	0.0582 g.

In several determinations the ordinary sodium chloride found in the laboratory was substituted for the C. P. salt, giving results as follows:

F present....	0.0344 g.	0.0543 g.	0.0688 g.	0.0866 g.	0.1094 g.
NaCl present 2 g.	2 g.	2 g.	2 g.	2 g.	3 g.
F found.....	0.0331 g.	0.0281 g.	0.0585 g.	0.0643 g.	0.1057 g.

These values serve to show that the influence of slight amounts of impurities in the sodium chloride was considerable.

In the place of sodium chloride, pure potassium chloride was used, giving:

F present....	0.0301 g.	0.0343 g.	0.0344 g.	0.0387 g.	0.0585 g.	0.0619 g.
KCl present. 4 g.	4 g.	4 g.	4 g.	4 g.	4 g.	4 g.
F found.....	0.0304 g.	0.0341 g.	0.0347 g.	0.0387 g.	0.0587 g.	0.0630 g.

Hence, potassium chloride recommends itself quite as well as sodium chloride.

Attempts were made to apply this volumetric method to the analysis of fluorspar. The powdered mineral was fused with silica and sodium-potassium carbonate. The silica was precipitated by ammonium carbonate and ammoniacal zinc oxide. The resulting solution was neutralized, diluted to 30 cc., 4 g. of potassium chloride added, and titrated with standard ferric chloride solution. No satisfactory end point could be obtained.

The Guyot-Greeff volumetric method seems admirable for simple solutions of sodium fluoride, but fails when other substances are present.

Starck and Thorin² have suggested the addition of a known volume of standard ammonium oxalate before precipitating with calcium chloride, with the idea that the presence of oxalate would render the calcium fluoride precipitate more insoluble and at the same time aid in its filtration. The combined precipitates were brought upon a Gooch crucible, dried and weighed according to the original directions. The known weight of the calcium oxalate was subtracted from the total. Results:

F present.	CaC ₂ O ₄ present.	CaF ₂ + CaC ₂ O ₄ found.	CaF ₂ found.	F found.
0.0344 g.	0.1097 g.	0.1787 g.	0.0690 g.	0.0336 g.
0.0344	0.1097	0.1786	0.0689	0.0335
0.0344	0.1097	0.1796	0.0699	0.0340

¹ *Ann. chim. appl.*, 1, 441 (1914).

² *Z. anal. Chem.*, 51, 14 (1912).

It was found preferable to determine the strength of the ammonium oxalate solution by precipitation and weighing as calcium oxalate, rather than by titration with permanganate. The numerical results of Starck and Thorin are verified, but the combined precipitate of calcium fluoride and oxalate was found extremely difficult to filter and handle, contrary to the observations of the original proposers of this modification. The method is obviously limited to the estimation of fluorine in neutral solutions of soluble fluorides in the absence of most other substances.

Precipitation as Thorium Fluoride.—Thorium fluoride is precipitated in gelatinous form, but becomes rapidly granular and easy to filter on standing. A further advantage lies in the fact that simple ignition transforms it to dioxide, in which form it may be weighed. The fluoride must be precipitated, moreover, in strictly neutral solutions. The best results obtained were far from satisfactory.

F present.....	0.0688 g.	0.0344 g.	0.0344 g.
F found.....	0.0661 g.	0.0368 g.	0.0329 g.

Some doubt was felt whether simple ThF_4 could be precipitated from a solution of sodium fluoride without being accompanied at the same time by Na_2ThF_6 . A solution of about 0.5 g. of sodium fluoride was treated with an excess of thorium nitrate in neutral solution. The washed precipitate was dissolved in acid, the thorium precipitated by ammonia, and from the filtrate a small amount of sodium chloride was obtained.

A number of characteristic reactions for the metals are known, upon which the presence of fluorine exercises an inhibitory influence. Steiger's¹ method, improved by Merwin,² takes advantage of the color produced on treating a titanium solution with hydrogen peroxide. Fluorine tends to destroy this color. This "fading" effect can be readily measured by comparing the depth of color of two equivalent titanium solutions, one of which contains the fluorine, while the other does not. This indirect method was worked out in the U. S. Geological Survey for analysis of fluorine-containing minerals and, as pointed out by the authors, is only applicable to fluorine in very small amounts. They also emphasize the necessity of each analyst carefully setting for himself standard conditions and developing a factor which shall satisfy his own conditions of operation.

To calculate the factor: About 0.02 g. of calcium fluoride was taken, fused with silica and 1 g. of sodium carbonate, extracted with water and the silica precipitated with ammonium carbonate. To the solution were added 3 cc. of hydrogen peroxide, 10 cc. of titanium sulfate (= 0.01 g. TiO_2), 6 cc. of sulfuric acid and the whole diluted to 100 cc. Its depth of color was compared by means of a Duboscq colorimeter with another titanium solution prepared under the same conditions, but containing no

¹ THIS JOURNAL, 30, 219 (1908).

² *Am. Jour. Sci.*, [4] 28, 119 (1909).

fluorine. A blank reading to provide for the influence of sodium sulfate gave the number 103. Substituting in the formula, $\frac{R - 103}{X} = \text{grams}$ of fluorine, the following readings gave:

Calcium fluoride.	F present.	Ratio R.	Factor X calculated.
0.0142 g.	0.0068 g.	120	2500
0.0182	0.0088	125	2500

Using this formula, $\frac{R - 103}{2500}$, the following results were obtained:

Calcium fluoride.	F present.	Ratio.	F calculated.
0.0230 g.	0.0115 g.	132	0.0116 g.
0.0389	0.0188	150	0.0188

These figures show that under standardized conditions reliable results can be expected. A less-concentrated titanium solution provides for still smaller amounts of fluorine. On a qualitative basis alone, the method stands as probably the only satisfactory means of detecting in a silicate amounts of fluorine less than a milligram.

Fluorine likewise produces a fading effect upon the color produced between a ferric salt and ammonium thiocyanate. The red color is more suitable for comparison than the titanium color and it was thought would lend itself to the detection of larger amounts of fluorine. A preliminary study was made into the extent to which the thiocyanate color would be affected by reagents other than fluorides.

Solutions were prepared as follows: A solution of alum (1 cc. = 0.01 g. of Al_2O_3), a solution of sodium silicate (1 cc. = 0.01 g. of SiO_2), a solution of microcosmic salt (1 cc. = 0.005 g. of P_2O_5). The effect of each of these common constituents of rocks, *i. e.*, Al_2O_3 , SiO_2 , P_2O_5 , was tried in turn upon a solution containing 10 cc. of ferric chloride (= 0.03 g. Fe_2O_3) and 5 cc. of 5% solution of ammonium thiocyanate, diluted to 50 cc. and compared with a standard prepared under similar conditions.

TABLE VI.

Al_2O_3 .		SiO_2 .		P_2O_5 .		Na_2CO_3 neutr. w. HCl.		NaF.	
Amount.	Ratio.	Amount.	Ratio.	Amount.	Ratio.	Amount.	Ratio.	Amount.	Ratio.
1 cc.	112	3 cc.	100	1 cc.	114	1 g.	102	0.0004	124
2	150	10	140	2	226	3	113	0.0007	128
5	271	20	148	3	decolor-	5	125	0.0010	142
10	350		ized	0.0014	161
..	0.0018	166

These values with NaF arrange themselves along a curve which could be used in reading the unknown amount of fluorine present necessary to produce a given fading effect, but the decided deleterious influence of the phosphorus, alumina, etc., which usually accompany fluorine in minerals shows the reaction not well adapted to such a field. It was further de-

terminated that the thiocyanate color is not a permanent one. Exposed to light, a solution was found to lose one-half its depth of color in 48 hours.

The halogens, chlorine, bromine and iodine when passed through a tube over samples of fluorspar heated to redness in a boat produced no reaction with the mineral. It is known that hydrochloric acid gas will transform sodium fluoride to sodium chloride. The effect of this gas was tried upon fluorspar.

The powdered mineral was placed in a platinum boat and heated in a fairly rapid stream of hydrogen chloride for 5 hours. To determine if the decomposition was complete, the contents of the boat after the operation were treated with water, when the calcium chloride formed dissolved. A high temperature was found necessary. At 350° the mineral was only very slightly decomposed. The amount of decomposition increased with higher temperature. At 500° after most of the mineral had been acted upon the resultant calcium chloride fused, occluding in the fused mass undecomposed mineral and the action ceased. At 450° the action was extremely slow and after 8 hours showed still only partial decomposition. None of eight different samples, weighing 0.1 to 0.2 g. subjected to hydrogen chloride gas were more than partly acted upon. Apparently that temperature could not be found, high enough to cause complete reaction with hydrochloric acid, and low enough to prevent fusion of the calcium chloride.

The mineral cryolite behaved in a different manner. A sample of 0.1380 g. heated at 600° in hydrogen chloride for $6\frac{1}{2}$ hours left a residue weighing 0.0875 g. which dissolved in a few drops of water to a clear solution. A second sample of 0.1252 g. at 650° for 6 hours left a residue of 0.0823 g. and dissolved completely. The aluminum chloride formed volatilized completely and carried with it some of the sodium chloride.

Lenz,¹ desiring to estimate the amount of fluorine in an organic compound, heated the substance with calcium oxide and after extraction with dilute acetic acid weighed calcium fluoride. Kessler² applied this method to sodium and ammonium fluorides. The principle employed recalled the J. Lawrence Smith method for alkalis; an attempt was made to use this to aid in the decomposition of fluorides not decomposable by sulfuric acid. A sample of topaz, finely powdered, was intimately mixed in a mortar with ten times its weight of calcium carbonate and three times its weight of ammonium carbonate. This was heated in a covered crucible for 15 minutes with a small flame, and for 15 minutes more to intense redness. The fluorine, it was thought, was now entirely transformed into calcium fluoride and the mass free from carbonate. It was powdered and placed with anhydrous copper sulfate and sulfuric acid in the apparatus

¹ *Ber.*, 12, 580 (1879).

² *Monatsh.*, 28, 163 (1907).

for estimating fluorine by the Offermann method. The conditions of preliminary ignition were varied in a number of trials, but the best results were always low.

Topas present.	F found.	F found.	F present.
0.2380 g.	0.0414 g.	13.9%	17.48%
0.2487	0.0369	14.8	...
0.2240	0.0321	14.4	...
0.2449	0.0352	14.4	...

This procedure failed to produce a successful method for fluorine. The ignition with calcium carbonate evidently led to the formation of calcium silicate. It is interesting to note that strikingly low results were likewise obtained when this substance in the form of wollastonite was applied to the Offermann method.

Additional Observations.—It is possible that some other metallic fluoride than those usually used might be adapted to an analytical method. The existing data upon the properties and solubilities of the fluorides is extremely meager. The fluorides of most of the metals were examined. Many of those generally regarded as insoluble were found not quantitatively insoluble, while practically all were formed as gelatinous precipitates quite impossible to filter and wash. Barium fluoride has been used by Gautier¹ in a special method for fluorine in mineral water. Cerium fluoride seemed to recommend itself, since on ignition it is transformed to the dioxide. It was found necessary to precipitate the fluoride of cerium in a solution absolutely neutral. The precipitate formed was almost colloidal and the weights of cerium oxide obtained always low.

There are other volatile compounds which might be employed other than silicon tetrafluoride. Jannasch² expels as hydrofluoric acid and collects in alkali; an elaborate piece of platinum apparatus is required which is almost prohibitive. The fluorine is then precipitated and weighed as calcium fluoride. The "etch" methods likewise involve the evolution of hydrogen fluoride. The consequent measurement in some way of this etching effect is hardly to be favored as an analytical method.

Boron fluoride is formed upon treating a fluoride with sulfuric acid in the presence of boric anhydride. In attempting to carry this out under conditions corresponding to those of the Offermann method for silicon tetrafluoride, it was found that silicon fluoride was likewise formed in the glass decomposition flask, and carried along with the boron fluoride to the absorption tube forming both H_2SiF_6 and $HB F_4$, incapable of being estimated by a simple titration. Hydrofluoric acid likewise forms a volatile ethyl ester which might be applied if some simple method of forming it analytically could be found.

¹ *Compt. rend.*, 152, 546 (1911); 154, 1670, 1753 (1912); 154, 1469 (1912).

² *Z. anorg. Chem.*, 9, 267, 273 (1895).

Summary.

It may be concluded from the preceding experiments:

1. That by means of a refusion with carbonate all the fluorine in silicate minerals can be accounted for by the Berzelius-Rose method.
2. That the conditions have been indicated according to which the best results can be obtained in the volatilization of silicon tetrafluoride by the Offermann method. This method is to be preferred for the direct estimation of fluorine in fluorspar.
3. That the soluble fluorides can be most accurately determined by precipitation as lead chlorofluoride.
4. That the only satisfactory method of determining and detecting fluorine in small quantities in minerals is the colorimetric method of Steiger-Merwin.

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[FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

AN ACID-RESISTING ALLOY TO REPLACE PLATINUM IN THE CONSTRUCTION OF A BOMB CALORIMETER.

By S. W. PARR.

Received July 26, 1915.

In the construction of an oxygen bomb for calorimetric purposes the necessity of providing an interior surface, such as is afforded by a platinum lining, is a recognized essential under all circumstances, but especially important in the combustion of Illinois and related coals, where the nitrogen and sulfur result in the formation of a mixture of nitric and sulfuric acids, equivalent on the average to about 30 cc. of 0.05 *N* nitric acid. If a solvent action with the metal of the bomb occurs, the error is two-fold, in that a too low correction for the total acid is indicated, thus increasing the heat credited to the fuel, and besides, any heat of solution developed by such action goes as a false credit to the fuel also and cannot be corrected for. The conditions as thus outlined would very naturally suggest the desirability of devising a metal or a complex which should be as resistant to the action of acids as platinum.

In arranging a working program where so little of the underlying principles have been developed, about the only method of procedure is the purely empirical one of trying many things. If we look for suggestions toward the theories proposed for the passivity of metals, we are impressed with the fact that investigators in that field are far from agreed as to what causes passivity. At best, however, passivity is only a transient condition and would seem not to be applicable to the problem in hand.

Another possible basis of procedure was formulated from reasoning somewhat after this fashion. There are many combinations of metals and metalloids having solubility characteristics quite different from the

metals which enter into the compound. Or perhaps, to put it differently, we have a much wider range of insoluble substances among compounds of metals with nonmetals than among metals themselves. For example, in Family VI of the Periodic Table we have oxygen, sulfur, selenium, tellurium. Now among the metallic oxides we have some extremely insoluble compounds as silicon dioxide, aluminium oxide, tin oxide, etc. But these compounds are brittle, or have no metallic properties which fit them for use where toughness or malleability are essential.

Take another combination. In Family IV we have silicon, more metallic in its properties than oxygen. If we combine silicon with iron up to say 17% of silicon, we have a silicide of iron, which is noted for its resistivity to solvents. While it melts and casts readily and has many applications in the arts, it is an extremely brittle substance and of such a very high degree of hardness that machining is impossible.

In the more metallic subdivision of Family VI we have chromium, molybdenum and tungsten, elements which have many nonmetallic properties and combine with oxygen to form acid radicals for many salts. They have also distinctively metallic properties, most pronounced so far as ductility is concerned in the case of tungsten, less so with chromium. If now we select certain metals which are notable in such characteristics as toughness and malleability, and which are at the same time in themselves somewhat resistant to acids, we might find some combinations which would retain or accentuate the insoluble feature of both constituents and have also a sufficient amount of toughness for working with machine tools. The metals which would naturally suggest themselves in this connection would be nickel, cobalt and possibly iron.

One further point may be noted. If we arrange the elements in an electrochemical series, and consider hydrogen as the dividing line between the electronegative and the electropositive substances, we shall find situated about midway between oxygen at the extreme electronegative end and hydrogen these four elements, chromium, vanadium, molybdenum, tungsten. Similarly, if we proceed from hydrogen towards the extreme electropositive end, we shall find about midway the elements cobalt, nickel, iron. Now we might attempt to satisfy the ionization viewpoint by reasoning in this fashion; here is an electronegative group, chromium, molybdenum, etc., which may be made to enter into combinations with certain members of the electropositive group in such a way as to neutralize or lower the ionization tendency of the metal to the vanishing point.

However hypothetical, or better perhaps however vague this line of reasoning, it served as a starting point. The first studies, therefore, were made on a nickel chrome series in which the chromium varied from 5-20%, the remainder being nickel. Solubility tests were very encour-

aging throughout the series, but there was a marked increase of resistivity with the higher percentage of chromium, that is, the 80 Ni and 20 Cr series. An attempt was made to produce a casting using this proportion. The difficulties encountered were serious and have constituted the most troublesome feature to master, aside from the development of the actual composition of the alloy. Three characteristics were especially in evidence at this point: first, the high melting point of the mixture; second, the unusual amount of shrinkage at the moment of solidifying; and third, the coarsely crystalline texture of the metal. The attempt to pour the 80-20 member of the series into a molded form resulted in the production of a casting which, in places, had more the property of a sieve than of a solid metal.

A series was next devised in which it was sought to introduce a third metal which might lower the melting point without decreasing the resistivity of the mixture. Copper was selected for this purpose chiefly because of its relatively low melting point. It is readily soluble in nitric acid, however, and it was considered probable that it would lower the resistivity of the series. Up to a certain point, however, the opposite proved to be true. The copper was made to vary in amount from 5-30%. The action of the acid was less evident up to a maximum of about 10%.

This is a point of fundamental importance and furnished a decided argument for a study in detail of the ternary series thus represented. This is now being carried on and cannot be dwelt upon here. Encouraged by the experience with copper, two more metals were tried out, such as might be used to advantage in the molten bath to clear it of dissolved gases and thus reduce the flaws in the cast metal. In this way the limit for aluminium and manganese, separately or together, was found to be about 2%.

Notwithstanding the progress that would seem thus to have been made in the direction of lowering the melting point, the metal was still coarse-grained in its fracture and seemingly could not be cast into usable forms. The fracture is shown in No. 7 of Fig. 1. The charge for the melt consisted of Ni = 75%, Cr = 20%, Cu = 5%.

However, the honey-comb feature frequently in evidence in the earlier castings had given way to a better texture, but there were still minute



No. 7.



No. 14.



No. 21.

Fig. 1.

openings or pin-holes which would prevent the use of the metal in a high pressure gas container.

The next modification which produced any noticeable improvement was secured by use of a formula as follows:

Ni.....	70 parts
Cr.....	20 parts
Cu.....	10 parts
Al.....	2 parts
Mn.....	1 part

The close-grained character of the metal is shown in the fracture of No. 14, Fig. 1. While the pin-holes were in evidence when a casting of this composition in the form of a bomb was put under 30 atmospheres pressure, still the extent of the porosity was sufficiently reduced to afford encouragement for continuing the experiments.

In devising the next series the experience so far seemed to indicate that the further addition of some metal might result advantageously but this time it was decided to go to the electronegative side and take a near relative of chromium. In test No. 21, therefore, there was added four parts of metallic tungsten. The effect of this addition was noticeable at once in the fracture of the metal which was now very fine-grained instead of coarse, No. 21, Fig. 1, and for the first time a serviceable casting free from pin-holes was produced. It was small and of simple form, being intended as a cover for an old platinum lined bomb. As thus put into use it proved to be exceedingly satisfactory.

Test No. 23 was cast in similar form and mixture, and proved to be free from pin-holes. Moreover, the resistivity to acid action was the best so far obtained. In the accompanying microphotographs the change in the texture of the metal is shown by comparing test No. 8 with No.



No. 8. Etched 3 min. in 1% FeCl_3 in 1:1 HCl $\times 60$.

Fig. 2.



No. 23. Etched 1 min. in 1% FeCl_3 in 1:1 HCl $\times 60$.

Fig. 3.

23. In No. 8, Fig. 2, the composition was the same as that used in test No. 7 of Fig. 1, while in No. 23, Fig. 3, the composition was the same as that used in No. 21, Fig. 1.

A much more difficult problem still remained so far as casting the metal was concerned in attempting to produce the main body of the bomb, about 5 kilos in weight, in perfectly homogeneous form. This was secured in test No. 40, and the finished bomb was put into commission about February, 1912, since which time it has served in more than 1500 combustions, without evidence of corrosion. Many of the determinations were made parallel with the platinum-lined bomb and the results show conclusively that in actual service the alloy bomb gives results equivalent in every respect to those indicated by the platinum lined outfit. In Table I are shown the acid titration values as obtained from the two instruments at such times as they were run parallel during the years 1912 to 1914, inclusive. For convenience the new alloy is referred to as "Illium." It will be seen that in 31 determinations the illium bomb titrations were in excess. In 15 cases the platinum outfit gave the higher titrations. In no case, however, is the acid value from the illium bomb sufficiently low to indicate a solubility effect. Indeed the variations are only such as might normally occur in the use of the same apparatus.

TABLE I.—ACID TITRATION VALUES (IN CC. OF STANDARD ALKALI) ILLUSTRATING RESISTIVITY OF AN ILLIUM ALLOY BOMB (I) COMPARED WITH THAT OF PLATINUM-LINED BOMB (PT).

I....	86.3	37.2	39.2	49.6	39.9	59.5	32.8	46.6	65.7	65.7	47.8	43.6
Pt....	76.2	41.5	42.9	51.6	41.4	55.8	31.7	44.7	59.0	43.1	39.9	38.2
I....	20.6	40.6	39.4	44.0	46.0	41.9	40.9	31.8	41.6	44.4	41.2	26.2
Pt....	22.1	36.7	36.5	40.1	41.3	38.0	42.7	30.5	39.7	37.0	45.4	31.0
I....	26.3	45.5	46.4	29.4	39.0	41.2	40.6	40.5	31.5	44.0	40.6	39.4
Pt....	20.9	38.5	44.5	29.8	38.0	42.5	36.4	35.5	37.0	40.1	36.7	36.5
I....	43.9	42.1	38.2	46.0	29.4	23.2	16.6	20.4	15.4	20.8	21.6	
Pt....	42.4	37.2	36.4	41.5	29.8	24.9	15.5	20.0	18.4	21.6	22.8	

The properties of the metal are further indicated by the accompanying illustrations. Fig. 4 shows the cover made from test No. 23. This cover has been used on the bomb shown in Fig. 5 made from test No. 40. Fig. 6, showing the lathe chips, affords a good illustration of the working properties of the metal.

The method adopted for measuring the action of acids was as follows: Test pieces were prepared having as nearly as possible a superficial area of 10 sq. cm. The strength of acid employed was 4 *N* nitric and the loss of weight was determined after a submergence in the acid for 24 hours. Calculations were then made of the loss in weight per hour for

a surface of 100 sq. cm. On this basis test piece No. 23 gave a loss of 0.03 mg. This degree of resistivity has been easily maintained in subsequent work and indeed improved upon. Standard pieces for corrosion tests gave results from six out of the last seven melts in which there was no weighable loss after 24 hours' contact with 25% nitric acid.

Some idea of the difficulty attending the casting of this material may be inferred from the fact that the first perfect casting, No. 40, was obtained in December, 1911. The next perfect result was No. 96 and was obtained about May 1, 1913, and not until over two years from this latter date did it seem possible to obtain perfect castings at will.

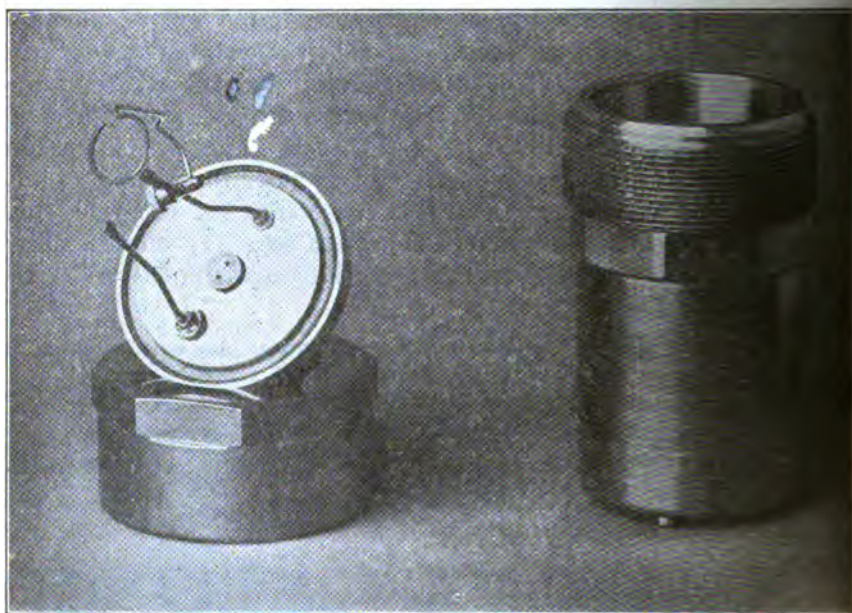


Fig. 4.

Fig. 5.

Not a little help in solving these difficulties has come from further experiments in varying the composition of the alloy. One other member of the chromium family has been added to advantage; namely, molybdenum. It may be used up to 6% of the mixture either with or without the tungsten. It increases the resistivity to acids but lessens slightly the toughness and tensile strength. The metal is more dense and less liable to flaws of the pin-hole type. With tungsten and no molybdenum present the metal draws easily into wire, having a tensile strength of 124,000 pounds per square inch. In cast form the tensile strength, using tungsten in the mixture, is from 55,000 to 60,000 pounds per square inch. Where

lybdenum is used, the tensile strength is from 50,000 to 55,000 pounds per square inch.

A temperature of approximately 1600° is necessary to secure a perfect melt. As might be expected, the dissolved gases are troublesome and



Fig. 6.

must be thoroughly removed before pouring. For this purpose from 1 to 2 parts of silicon-copper, manganese-titanium, and aluminium are added, stirring the mixture well with a rod of pure nickel. A small amount of cryolite and boron suboxide are also added as a flux. On account of the high temperature employed graphite crucibles are necessary, but

MELT No. 117.

Percentage Composition of Illium Alloy. Analytical Results by F. E. Rowland and S. A. Braley.

Cu.....	6.42
Mn.....	0.98
Si.....	1.04
W.....	2.13
Ni.....	60.65
Al.....	1.09
Fe.....	0.76
Cr.....	21.07
Mo.....	4.67

Total..... 98.81

they must have a lining of silicious material, owing to the readiness with which carbon is absorbed by the molten material.

The analysis of the product requires a special study of methods. This has been carried out with fairly satisfactory results. The composition of a representative sample was found as shown in the preceding table.

No determination thus far has been made for carbon, boron or titanium.

URBANA, ILLINOIS.

A CORRECTION.

In an article entitled, "Can the Dissociation Theory be Applied to Solid Solutions in Steels?" which appeared in the September number of THIS JOURNAL, the specific resistances of the steel which had been hardened and subsequently reheated to different temperatures were given. In order to render the values as near the absolute value as possible corrections to the observed values necessitated through the calibrations of the recording instruments were made. The corrections expressed in microhms due to the high reading of the ammeter used amount in the present case to from 0.21 to 0.24 microhms, according to the specific resistance. As the ammeter read too high these corrections should have been subtracted from the observed values, but by mistake the corrections were in all cases added. In order, therefore, to reduce the values reported to their true value, from 0.42 to 0.48 microhms should be subtracted from the figures given in the table. This correction would in no way affect the significance of the results or any deductions drawn therefrom.

E. D. CAMPBELL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

HEXABROMODIACETYL.

By C. LORING JACKSON AND ROGER ADAMS.

Received August 28, 1915.

In an earlier paper¹ A. H. Fiske and one of us described two acids, one melting at 207°, the other at 174°, made by the action of sodium hydroxide on tetrabromo-*o*-quinone, and it was also stated that, when treated with bromine and water, these acids were converted into a yellow diketone, to which the formula $\text{CBr}_3\text{CHBrCOCOCBr}_3$ was assigned. On continuing the study of this compound we have found that this formula is not the true one, but that it is really the hexabromodiacetyl $\text{CBr}_3\text{COCOCBr}_3$. The data on which this conclusion rests are given in Table I containing all the analytical results obtained by us from the substance itself and its principal derivatives. The first column gives the percentages calculated for $\text{CBr}_3\text{CHBrCOCOCBr}_3$, the second the data obtained by

¹ *Am. Chem. J.*, 50, 341 (1913).

Dr. Fiske in the earlier part of the work, the third those obtained in the work described in this paper, and the fourth the percentages calculated for $\text{CBn}_2\text{COCOCBr}_2$.

TABLE I.

	1. CBnCHBrCOCOCBr_2	2. Fiske.	3. Adams.	4. $\text{CBn}_2\text{COCOCBr}_2$
Br.....	85.90	85.78; 86.00	85.88	85.70
C.....	9.20	9.84; 9.47	8.62	8.57
H.....	0.15	0.58; 0.50	0.40	0.0
MW.....	653	514; 512 ¹	560
Methyl Alcohol Addition.				
	$\text{CBnCHBrCOC(OHOC}_2\text{H}_5\text{)CBn}_2$			$\text{CBn}_2\text{COC(OHOC}_2\text{H}_5\text{)CBn}_2$
Br.....	81.75	81.21; 81.32	81.17; 81.01; 81.27 ²	81.08
C.....	10.51	10.52	10.26	10.14
H.....	0.73	0.97	0.86	0.68
MW.....	685	584; 588; 601 ²	592
Ethyl Alcohol Addition.				
	$\text{CBnCHBrCOC(OHOC}_2\text{H}_5\text{)CBn}_2$			$\text{CBn}_2\text{COC(OHOC}_2\text{H}_5\text{)CBn}_2$
Br.....	80.11	80.17; 79.75	79.30; 79.11; ³ 79.52	79.20
C.....	12.01	12.35	12.01; 11.99	11.88
H.....	1.00	1.25	1.12; 1.09	0.99
MW.....	699	597; 582	606
Benzyl Alcohol Derivative.				
	$\text{CBnCHBrCOC(OHOC}_2\text{H}_5\text{)CBn}_2$			$\text{CHBr}_2\text{COC(OHOC}_2\text{H}_5\text{)CBn}_2$
Br.....	70.48	67.89; 68.29	68.01 ⁴	67.92
C.....	21.12	22.58	22.43	22.42
H.....	1.32	1.90	1.77	1.53
MW.....	681	580; 575; 577	589
Acetone Reductions.				
	$\text{CHBr}_2\text{COCOCBr}_2$			$\text{CHBr}_2\text{COCOCBr}_2$
Br.....	80.81	79.68; 79.80; 79.58 ⁵	79.60
MW.....	495	375; 383	402
	$\text{CHBr}_2\text{COC(OHOC}_2\text{H}_5\text{)CBn}_2$			$\text{CHBr}_2\text{COC(OHOC}_2\text{H}_5\text{)CBn}_2$
Br.....	77.41	76.02; 76.43 ⁶	75.91
C.....	13.55	13.86	13.67
H.....	1.29	1.54	1.32
MW.....	620	502	527

¹ Subs. 0.7705, 1.3457, Δ 0.57, 1.0, C_6H_6 12.874. Subs. 0.3010, 0.2348, AgBr 0.6074, CO_2 0.0742, H_2O 0.084.

² Subs. 0.1483, 0.1987, 0.2394, 0.3090, AgBr 0.2829, 0.3783, 0.4571, CO_2 0.1162, H_2O 0.0241. Subs. 0.2151, 0.4482, 0.6655, Δ 0.15, 0.31, 0.45, C_6H_6 12.290.

³ Subs. 0.1515, 0.1449, 0.1210, 0.2324, 0.2523, 0.2256, 0.5057, AgBr 0.2823, 0.2693, 0.2261, CO_2 0.1024, 0.1110, H_2O 0.0235, 0.0248, Δ 0.15, 0.345, C_6H_6 12.580.

⁴ Subs. 0.1602, 0.2457, 0.2292, 0.4267, 0.7335, AgBr 0.2560, CO_2 0.2021, H_2O 0.0393, Δ 0.165, 0.31, 0.53, C_6H_6 11.971.

⁵ Subs. 0.1918, 0.1529, 0.1271, 0.2465, 0.6717, AgBr 0.3591, 0.2866, 0.2381, Δ 0.27, 0.72, C_6H_6 12.164.

⁶ Subs. 0.1427, 0.1416, 0.2230, 0.1850, AgBr 0.2549, 0.2543, CO_2 0.1133, H_2O 0.0309, Δ 0.135, C_6H_6 13.639.

This table brings to light the astonishing fact that the percentages calculated for the two formulas of the diketone and its methyl and ethyl hemiacetals differ by less than 1%, so that it is impossible to distinguish between them by these analyses, and further that the data at hand, when the earlier paper was written, justified the adoption of the heptabromomethyldiacetyl formula instead of that of the hexabromodiacetyl, since the results from the benzyl compound, which alone told against it, remained unintelligible until our later work had shown the ease with which bromine is replaced by hydrogen in these substances.

When at last the nature of this benzyl derivative was understood, it became one of our strong arguments in favor of the hexabromodiacetyl formula, which was established without question by the molecular weight determinations, the analyses of the other reduction products, and especially by the fact that the compound formed from it by the action of acetone was identical with tetrabromodiacetyl made from bromine and diacetyl in its melting point 94–95° (uncorr.), and in its very characteristic yellow coffin-shaped crystals. The heptabromomethyldiacetyl and its derivatives therefore must be struck from the list of known compounds.

So far as we can find, hexabromodiacetyl has been prepared only from tetrabromo-*o*-quinone as described in this paper. Some attempts of our own to prepare it with bromine and diacetyl led only to the known tetrabromodiacetyl in confirmation of the work of our predecessor,¹ and when we tried to introduce more bromine into this substance by exposing a mixture of it with bromine to the sunlight, no action was observed. Upon heating the mixture in a sealed tube an action took place, but the product was so tarry that we did not continue our experiments in this direction.

The most striking property of the hexabromodiacetyl is the ease, with which it forms the monomethylhemiacetal $\text{CBr}_3\text{COC}(\text{OHOCH}_3)\text{CBr}_3$, melting at 105° (uncorr.), or the corresponding ethyl compound melting at 96–97° (uncorr.) by standing in the cold with the alcohol.²

So far as we know, these are the first hemiacetals prepared from diketones with open chains, but such compounds have been obtained from ring diketones and the closely related para and orthoquinones.³ This easy formation of hemiacetals from hexabromodiacetyl $\text{CBr}_3\text{COCOCBr}_3$ seemed to us to deserve study, but we have had time to try only a few experiments, and therefore all the statements which follow are liable to revision after a fuller study of this subject. It seems probable that the

¹ Keller, *Ber.*, 23, 35 (1890).

² *Am. Chem. J.*, 50, 367 (1913). The melting points in this earlier paper are somewhat lower than those given above, which is principally due to our discovery that petroleum ether is an almost perfect solvent for these compounds.

³ Zincke, Arnst, *Ann.*, 267, 319, 331; Jackson, Grindley, *Am. Chem. J.*, 17, 579 (1895); Jackson, MacLaurin, *Ibid.*, 38, 127 (1907); Jackson, Flint, *Ibid.*, 39, 80 (1908).

diketone structure is more favorable to the formation of hemiacetals than the ketone, since we were unable to make one by the action of alcohol on pentabromoacetone; but in spite of this the diketones apparently stand at the bottom of the list of hemiacetal producing compounds, since it was necessary to have this structure reinforced by the 6 atoms of bromine, neither tetrabromodiacetyl, nor dibromodiacetyl, nor diacetyl itself showing any trace of the formation of a hemiacetal, when treated with alcohol. Aldehydes and quinones on the other hand need much less help from the presence of halogens, the monochloroaldehyde certainly forming a hemiacetal, and it is even possible that aldehyde itself does, although the evidence in this case is not convincing.¹ Tetraethoxy-*p*-quinone also forms an unstable hemiacetal, although in this case by the action of sodium alcoholate instead of alcohol, and both the para and orthoquinones give stable hemiacetals with much less halogen (2 to 3 atoms) than the diketone.

The hemiacetals derived from hexabromodiacetyl show a remarkable stability toward acids. In fact we have not succeeded in recovering the diacetyl from them, whereas chloral alcoholate is decomposed by strong sulfuric acid in the cold, and the hemiacetals of the paraquinones even by dilute hydrochloric acid at ordinary temperatures, while those of the orthoquinones, although more stable, yield to acids at higher temperatures. It is interesting that in these cases the greater stability belongs to substances with the carbonyls adjacent. In view of the easy formation of hydrates from substituted aldehydes it is strange that we have observed no sign of the formation of a hydrate from hexabromodiacetyl.

In all the hemiacetals isolated by us only one of the carbonyls of the hexabromodiacetyl was affected by the alcohol, but there are some indications that the action could extend to the other also, since, when the diketone stood for a long time with absolute methyl alcohol, a thick, red oil was obtained instead of the crystalline hemiacetal, and, when it was boiled with the alcohol, a less pure product resulted than in the cold. Both of these observations can be explained by the formation of a di-hemiacetal, but more experiments are necessary before this explanation is accepted. The orthoquinones show a similar tendency to form mono-hemiacetals.

We consider these compounds hemiacetals, because we can find no other way in which the alcohol could be attached to the diketone; and this view is supported by the formation of an oxalic ester in addition to bromoform² when the ethyl compound was decomposed with water at 100°. Some of their properties however, are different from those we should have expected of hemiacetals. For instance, their stability toward acids.

¹ Jacobsen, *Ber.*, 4, 215 (1871); Renard, *Ibid.*, 8, 132 (1875).

² *Am. Chem. J.*, 50, 368 (1913).

since they were not decomposed by boiling hydrobromic acid, or by dilute sulfuric acid boiling at 135° . At 150° the acid decomposed them, but no hexabromodiacetyl was recovered. Further acetic anhydride or acetyl chloride had no action on them in spite of the hydroxyl they contain. Although these properties are unexpected, they are not incompatible with the hemiacetal formula. These hemiacetals are somewhat more stable toward alkalis than the hexabromodiacetyl, but are decomposed by them with the formation of bromoform, and at least in the ethyl compound an oxalic ester. A greater stability is also shown by the fact that they are unaffected by hydriodic acid, which acts on the mother substance in a way to be described presently.

The hexabromodiacetylmonomethylhemiacetal was observed in 3 different sorts of crystals, when the solvent used was petroleum ether. (a) Long needles; (b) short broad square ended prisms, which may have been only a different habit of the first form; and (c) octahedra apparently of the tetragonal system, whereas the other two seemed to be orthorhombic. This last form also has a much more brilliant lustre than the others. All three melted at 105° (uncorr.), and could be converted into the first form by recrystallization. On the other hand the ethylhemiacetal was observed only in long narrow plates.

Benzyl alcohol acted on the hexabromodiacetyl in a more complex way than the fat alcohols, giving a compound containing only 5 atoms of bromine, for which we have worked out 2 constitutional formulas, either pentabromodiacetylmonobenzylhemiacetal $\text{CHBr}_2\text{COC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$, or benzyloxypentabromodiacetyl $\text{C}_7\text{H}_7\text{OCBr}_2\text{COCOCBr}_3$. We give the preference to the first of these formulas for the following reasons: the percentages of hydrogen found agree very well with this formula, but differ from that required by the second by a greater amount than is found in any other work by the two analysts who made them. The formation of a hemiacetal is characteristic of the behavior of the other alcohols with hexabromodiacetyl, whereas no other alkyloxy compounds have been observed. Hexabromodiacetyl undergoes the replacement of bromine by hydrogen also with acetone or hydriodic acid. The substance is more stable toward alkalis than the mother substance; this property is shown by other hemiacetals, whereas a substance with the second formula would probably be less stable. Alkalis give no bromoform with it.

Metanitrobenzyl alcohol did not combine with hexabromodiacetyl.

A few attempts to reduce the carbonyls in hexabromodiacetyl gave unsatisfactory results, but hydriodic acid converted it into tetrabromodiacetyl by replacing 2 atoms of bromine by hydrogen; and the same product was obtained more easily with acetone in the cold. If alcohol was mixed with the acetone, the product contained pentabromodiacetylmonoethylhemiacetal $\text{CHBr}_2\text{COC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$, melting at 115° (un-

corr.); but acetone mixed with methyl alcohol gave no replacement of bromine by hydrogen, the only product being hexabromodiacetylmonomethylhemiacetal.

In forming the pentabromohemiacetals the replacement of bromine by hydrogen would be likely to take place in the CBr_3 , next the unaltered carbonyl, if it happened after the formation of the hemiacetal (which is by no means established); and this view is supported by the observation that no bromoform could be detected, when the ethyl, or benzyl pentabromo compound was decomposed by an alkali, whereas the hexabromohemiacetals give bromoform under these conditions. We have therefore formulated these compounds accordingly.

When hexabromodiacetyl was treated with an aqueous solution of potassium iodide, iodine and carbonic dioxide were set free, and a new compound obtained, which melted with decomposition at $120-125^\circ$. We think that this substance is the triodobromoacetone $\text{Cl}_3\text{COCH}_2\text{Br}$, but cannot support this opinion by conclusive evidence. The discussion of this subject will be found in the Experimental Part.

The substance melting at $71-72^\circ$ mentioned in the previous paper¹ as formed by the action of water on the hexabromodiacetyl, and also as a secondary product in its preparation has been recognized as pentabromoacetone. It was also obtained by the action of perhydrol, or constant boiling hydrobromic acid at 100° on the hexabromodiacetyl. We are unable to understand the mechanism of these reactions, but they are not without analogy, as pentabromoacetone is also formed by the action of hydrogen dioxide on tetrabromodiacetyl.²

Experimental.

Preparation of Hexabromodiacetyl,³ $\text{CBr}_3\text{COCOCBr}_3$.—The process used by us differs in some important details from that described in the previous paper, and is therefore given in full. 200 g. of sodium hydroxide were dissolved in a litre of water, and after cooling to a few degrees above zero, 100 g. of tetrabromo-*o*-quinone were added in small portions at a time with constant shaking. If impure orthoquinone was used, the same product was obtained, but the yield was materially lowered. The green color, which appeared at first, gradually changed to brown, and at the same time enough gas was given off to cover the surface of the solution with foam. The mixture was allowed to stand in ice for 2-3 hours, and then at room temperatures for about 5 hours, after which it was poured into 400 cc. of strong hydrochloric acid (more than enough for neutralization) slowly and with constant cooling, so that the tem-

¹ Jackson, Fiske, *Am. Chem. J.*, 50, 366 (1913).

² Keller, Maas, *Centralb.*, 1898, I, 24.

³ This substance was supposed by Fiske and one of us to be heptabromomethyl-diacetyl (*Am. Chem. J.*, 50, 360 (1913)). See the introduction to this paper.

perature of the mixture should never rise above luke warm. The yellowish brown flocculent precipitate of tetrabromopyrocatechin formed in this way was filtered off after settling for 5-10 minutes. To the filtrate were added 2 cc. of bromine, and the mixture shaken, until it was entirely absorbed. This treatment was repeated, till the presence of an excess of bromine was shown by the reddish color of the liquid, which required 23-25 cc., if the tetrabromo-*o*-quinone was pure, 13-18 cc., if it was crude. During the treatment with bromine the red liquid became at first milky, then began to give off carbon dioxide, and toward the end of the process a yellow precipitate appeared. In 5-10 minutes after the end of the treatment this precipitate had settled, when it was filtered out, and allowed to stand on a porous plate until thoroughly dry, which took about a day. An additional amount of decidedly impure product was obtained by allowing the filtrate to stand over night with 5 cc. of bromine. The dry precipitate was powdered, and extracted with successive portions of petroleum ether (boiling 30-50°), until the yellow substance was completely removed leaving a brown, tarry impurity. Upon distilling off the larger part of the petroleum ether, and cooling the residue, the hexabromodiacetyl crystallized out in a pure state, as shown by its melting point 100-101°¹ (uncorr.), which was not raised by recrystallization from petroleum ether. The yield varied from 21 to 24 g. from 100 g. of tetrabromo-*o*-quinone, but fell as low as 12 g., if crude material was used. The analyses of this substance will be found in the introduction.

Properties of Hexabromodiacetyl.—It crystallizes from petroleum ether in orange yellow plates shaped like arrowheads, and melts at 100-101° (uncorr.) instead of at 97-98° as given in the previous paper. This difference is probably due to the removal of the tarry impurity left after repeated extractions with petroleum ether. It is easily soluble in alcohol, methyl alcohol, ether, benzene, carbon tetrachloride, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It is very stable toward acids, the three strong acids having no action on it in the cold, or on short warming to 100°. Fuming nitric acid when boiling dissolves it, but on cooling the substance crystallizes out to all appearance unaltered. Analyses showed however, that it had lost 1-2% of bromine. Boiling for several hours with strong nitric acid seems to decompose it completely. Boiling with sulfuric acid diluted with its own volume of water gives bromoform, but in such small amount that only a very slight decomposition is indicated. Water, hydric dioxide or constant boiling hydrobromic acid, while without effect on it in the cold, if heated with it to 100° in a sealed tube for 10 days, decomposes it, two of the products in each case being pentabromoacetone and bromoform. This behavior recalls the formation of penta-

¹ In the previous paper it was given as 97-98°.

bromoacetone in a yield of 30-40% from tetrabromodiacetyl by the action of hydric dioxide. It is certainly strange that the substance should be distinctly less stable with water than with sulfuric acid. Hydriodic acid or acetone reduces it, as will be described later, and so will the action of potassium iodide.

In the hope of obtaining a dicyanhydrine similar to that yielded by tetrabromodiacetyl 15 g. of the hexabromodiacetyl mixed with 2-3 cc. of ether and 40 g. of a 40% aqueous solution of hydrocyanic acid were heated to 40° under a return condenser. The solid gradually went into solution, and after 5-10 hours the two layers of liquid formed at first were converted into a homogeneous mixture, which was allowed to stand over night, heated for a few more hours in the morning, and after cooling to 0° diluted with its own volume of water, and extracted with ether. The dried extract yielded only a yellow oil, which did not solidify on cooling, or standing for a month, and yielded only an oil on saponification with hydrochloric acid at 100°.

Alkaline reagents on the other hand decompose it easily. The hydroxide of sodium, potassium, or barium even in dilute solution converts it rapidly into bromoform and an oxalate; sodium carbonate acts in the same way but more slowly. A quantitative study of this reaction made by Fiske and one of us showed that two molecules of bromoform and one of oxalic acid were formed. Hot sodium methylate gave the same result; but in the cold a colorless product melting at about 80° was obtained, which has not been investigated. Boiling with an aqueous solution of sodium acetate also gave bromoform hydrobromic acid and oxalic acid; but when boiled with calcium carbonate and water, a sharp odor like that of a bromoketone was observed, and only tarry products were obtained. The same odor was produced by boiling with silver and water, but in this case oxalic acid and silver bromide were detected. A mixture of aqueous ammonia and alcohol gave in the cold oxamide; and aniline added to a benzene solution of the diketone gave oxanilid. *o*-Phenylene-diamine gave somewhat impure *o*-phenyleneoxamide. Hydroxylamine hydrochloride had no apparent action; phenylhydrazine removed bromine from it; pyridine gave a black tar. No action was obtained with acetylchloride, or acetic anhydride, or benzoylchloride. Aqueous sulfurous acid did not act on it, even when standing several months with it. Zinc and acetic acid, or aluminum amalgam gave tars in preliminary experiments; but better results were obtained with hydriodic acid, as is described later. Bromine in the cold had no apparent effect upon it, and when heated with it in a sealed tube, tarry products were formed. The most interesting behavior of the diketone is that with alcohols, which is therefore described in detail.

Action of Hexabromodiacyl with Alcohols. Hexabromodiacylmonomethylhemiacetal, $\text{CBr}_3\text{COC}(\text{OHOCH}_3)\text{CBr}_3$.—This substance was prepared by allowing a solution of hexabromodiacyl in methyl alcohol to stand for 4–5 days. A less pure product was obtained by the aid of heat. Absolute methyl alcohol should not be used in this preparation, as it forms an oily substance; in fact in an experiment, which stood for 2 weeks, very little hemiacetal was obtained, the chief product being an unmanageable thick, red oil. Even with ordinary methyl alcohol a little of this oil was formed, and therefore after the methyl alcohol had evaporated spontaneously, the residue was allowed to stand on a porous plate, after which it was recrystallized from petroleum ether, until it showed the melting point 105° (uncorr.). Analyses of this substance are given in the table in the introduction. 10 g. of diketone yielded 5 g. of the hemiacetal.

Properties of Hexabromodiacylmonomethylhemiacetal.—Three sorts of crystals of this substance were obtained from petroleum ether, which differed so much in appearance that it certainly crystallizes in 3 different habits if not in 3 crystalline forms. On cooling, or rapid evaporation of the solution, most of the crystals are slender, long prisms, sometimes with a bluntly pointed end, sometimes with a square end; these turn opaque, when exposed to the air, but without loss of weight. The second form consists of short, square-ended prisms like slightly elongated cubes, usually bevelled on the edges, more rarely on the ends. These predominate when the evaporation is carried on slowly; but in most crystallizations both forms appear, and one is converted at least partially into the other by recrystallization. We do not feel certain that these are not different habits of the same crystalline form in spite of the great difference in their appearance. The third sort of crystal on the other hand seems distinctly to belong to a different system, for, while we should call the other two forms orthorhombic, or perhaps monoclinic, this third one seems to be tetragonal, since it consists of octahedra modified by many small planes, the two most conspicuous sets either truncating two opposite angles, or else the 4 edges of the octahedron the opposite angles then being unmodified. The vertical axis is but little longer than that of a regular octahedron, but in no case did we observe similar modifications on all the angles or edges. This form also has a much more brilliant lustre than the other two. We obtained it only once, and could not again find the conditions, under which it is formed. On recrystallization from methyl alcohol it is converted into the one first described. All three forms contain the same % of bromine.

The hemiacetal when crystallized from petroleum ether melts at 105° (uncorr.), but, if methyl alcohol is used, the melting point cannot be raised to this temperature, which explains the lower melting point ($100\text{--}101^\circ$)

given in the earlier paper. This is obviously due to an action of the methyl alcohol upon it, which was also shown by the fact that such a solution although colorless at first turned yellow in a few minutes, but from this solution colorless crystals were obtained. As already stated, absolute methyl alcohol, if allowed to stand with it for some weeks, converts it into a red oil. The most obvious explanation of this action is that the dihemiacetal is formed, but this is rendered doubtful by the facts that the benzene solution also turns yellow on standing exposed to the air, and upon evaporating the benzene solution used in the molecular weight determination the residue was brownish. The crystals show a tendency to turn brown, when exposed to the air especially if moist. This apparent instability is surprising in view of the fact that it offers a strong resistance to the action of acids, strong nitric acid dissolving it apparently unchanged, while it was not decomposed by sulfuric acid diluted with its own volume of water, until it had been boiled with it some time. Then it formed an oil smelling like camphor. It is easily soluble in all the common organic solvents except petroleum ether, in which it is less soluble. This is the best solvent for it. It distills slightly with steam. It is unstable toward alkalies since alcoholic ammonia forms ammonium bromide; and aniline gives an oil. Hydroxylamine hydrochloride, acetic anhydride, or acetyl chloride does not act on it. A methyl alcohol solution boiled with finely divided silver gives an oil and a few white crystals melting near 70° .

Hexabromodiacetylmonoethylhemiacetal, $\text{CBr}_3\text{COC}(\text{OHOC}_2\text{H}_5)\text{CBr}_3$.—Ten grams of hexabromodiacetyl dissolved in 150 cc. of alcohol were allowed to stand at ordinary temperatures for 2–3 days, after which the alcohol was allowed to evaporate spontaneously. If the solution was heated, the product was less pure. The yellowish white crystals thus obtained, after standing on a porous plate, were crystallized from petroleum ether, until they showed the constant melting point $96\text{--}97^{\circ}$. The yield after one crystallization was 6 g. The analyses will be found in the table in the introduction.

Properties of Hexabromodiacetylmonoethylhemiacetal.—It crystallizes in narrow plates often 2–3 cm. long terminated by two planes at different angles to the sides, less commonly by one of these planes, so that there is either a blunt, or a very sharp end, according to which of the planes is present. It turns brown easily, when exposed to the air, especially if moist; after this change the percentage of bromine had fallen about 2%. It melts at $96\text{--}97^{\circ}$ (uncorr.) instead of $93\text{--}94^{\circ}$ as given earlier. It is easily soluble in alcohol, methyl alcohol, ether, acetone, or ethyl acetate; soluble in benzene, chloroform, tetrachloride of carbon, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It distills with steam, although with difficulty.

When the monoethylhemiacetal was heated in a sealed tube with water to 100° for several days, the products were carbon dioxide, bromoform, hydrobromic acid, and probably monoethyloxalic ester, as the diethylester was obtained from it by distillation.¹

As this substance could be prepared more easily than the methyl compound, it was studied in greater detail, and we tried especially to convert it back again into the hexabromodiacetyl but without success. Four experiments were tried with boiling dilute sulfuric acid, in which the water was allowed to evaporate, until the boiling point had risen from 110 to 135° , and at this temperature the boiling was continued for some time under a return condenser. The ethyl compound turned slightly yellow, but was recovered unchanged in every case. On heating to 150° for a few hours with strong sulfuric acid the substance was decomposed, forming a dirty yellow solution, but no hexabromodiacetyl could be detected. Boiling with constant boiling hydrobromic acid for 3 hours, or heating with it to 100° in a sealed tube produced no change. This marked stability toward acids is striking in view of the ease, with which it decomposes when moist, or when heated with water.

Sodium hydroxide decomposes the hexabromodiacetylmonoethylhemiacetal giving bromoform and a little oxalate, while barium hydroxide acts in a similar way, but only a trace of oxalate is formed. Sodium carbonate gives over 10% more bromoform than that required for one molecule, but only about half the calculated amount of oxalic acid. Sodium methylate also decomposes it, even when used in the proportion of only one molecule. In all these reactions with alkaline substances it was observed that the hemiacetal is distinctly more stable than the diketone. Ammonia, or aniline forms only tars, but also acts slowly. Hydroxylamine hydrochloride had no action on it.

Acetic anhydride, or acetyl chloride dissolves the hemiacetal, but no reaction takes place even after standing 4-7 days. If sodium acetate is used with the acetic anhydride, a yellow color appears, but the slight decomposition is probably due to the action of the salt. When the substance is heated to 120° over night with acetyl chloride, a sweet swelling oil is obtained, which deposits crystals of the unchanged monoethylhemiacetal, but the amount which reacts is so small that we could not study the product. Acetic anhydride when hot also gives an oily derivative. Zinc and acetic acid give small amounts of oil. When the hexabromodiketone is heated with alcohol, instead of reacting with it in the cold, tarry products are obtained with an odor like that of a bromoketone.

Pentabromoacetone.—In the preparation of hexabromodiacetyl the filtrate from it was mixed with 5 cc. of bromine, and allowed to stand

¹ Anschütz, *Ber.*, 16, 2413 (1883).

over night, when a red oil was deposited, which changed to a sticky crystalline mass, if it was allowed to stand a few days in an open beaker, after the water had been separated. Most of the oil was then removed by a porous plate, and the residue crystallized by the slow evaporation of its solution in petroleum ether. The crystals were partly orange yellow hexabromodiacetyl, partly a white substance, which was separated mechanically, and after crystallization from petroleum ether melted constant at 73° (uncorr.). Although the melting point of pentabromoacetone is 76° , our analyses showed that our product is this substance.

Calc. for $\text{CBr}_2\text{COCBr}_2\text{H}$: C, 7.95; H, 0.22; Br, 88.31; M. W., 453. Found: C, 8.50; H, 0.46; Br, 88.30; M. W., 388, 413, 417.

The same compound was formed by heating hexabromodiacetyl for 10 days at 100° in a sealed tube with water, perhydrol, or constant boiling hydrobromic acid; bromoform was also formed in each case.

When hexabromodiacetyl stood for several days with amyl alcohol, the product, after being freed from unaltered alcohol by a blast of air, was a yellow oil, which to our great surprise contained an amount of bromine only 1% too high for that required by the monoamylhemiacetal.

Pentabromodiacetylmonobenzylhemiacetal, $\text{CBr}_2\text{HCOC}(\text{OHOC}_7\text{H}_7)\text{-CBr}_2$.—Five grams of hexabromodiacetyl were heated on the water bath in a 25 cc. flask with 5–6 g. of benzyl alcohol for 10 hours. At the end of this time the residue was distilled with steam, which carried over the excess of benzyl alcohol and the benzyl bromide formed. The yellowish oil, which had not distilled with the steam, was allowed to stand until it had crystallized, and then after being freed from oil with a porous plate it was crystallized from naphtha boiling between 70° and 100° , until it showed the constant melting point $109\text{--}110^{\circ}$ (uncorr.). The yield varied from 2 to 2.5 g. The analyses given in the introduction show that the substance is the pentabromodiacetylmonobenzylhemiacetal. The hydrobromic acid formed in this reduction was detected in the water, with which the product was distilled, and had also converted some of the benzyl alcohol into benzylbromide as was shown by its violent action on the eyes.

Properties of Pentabromodiacetylmonobenzylhemiacetal.—It crystallizes from ligroin in large, thick, rhombic prisms, which melt at $109\text{--}110^{\circ}$ (uncorr.). It is easily soluble in alcohol, methyl alcohol, ether, benzene, or glacial acetic acid; less soluble in ligroin, which is the best solvent for it; essentially insoluble in petroleum ether, or water. Strong sulfuric acid, nitric acid, hydrochloric acid, or hydrobromic acid has no apparent effect on it. It is more stable toward alkalis than the hemiacetals of hexabromodiacetyl, as barium hydroxide did not attack it at all even on standing with it for 2 days, and sodium hydroxide did not decompose it completely, until it had stood with it several days. The yellow oil thus obtained contained no bromoform. Acetyl chloride, or acetic an-

hydride has no action on it, in fact it crystallizes very well from the anhydride, the crystals showing the melting point $109-110^{\circ}$, and containing 67.93% of bromine (calc. for the hemiacetal 67.92).

Metanitrobenzyl alcohol when heated on the water bath with hexabromodiacetyl was converted into *m*-nitrobenzyl ether, and this was the only product found, the diacetyl having apparently decomposed completely. Phenol formed with hexabromodiacetyl an unpromising black mass.

Attempts to make hemiacetals by contact with alcohols yielded no results with tetrabromodiacetyl, dibromodiacetyl, diacetyl, benzil, or pentabromoacetone.

Reduction of Hexabromodiacetyl.—Reduction experiments with zinc and acetic acid, or sulfuric acid yielded only a few drops of oil; but acetone, or hydriodic acid gave a better result. Five grams of hexabromodiacetyl were dissolved in acetone, and allowed to stand 4–5 hours¹ at ordinary temperatures, after which the solution was allowed to evaporate spontaneously under the hood, because of the bromoacetone. On standing over night a hard mass was obtained, which after removing the last of the bromoacetone by a porous plate was crystallized from petroleum ether, until it showed the constant melting point $94-95^{\circ}$ (uncorr.). This suggested that it was tetrabromodiacetyl, which melts at this temperature. Accordingly a specimen of this compound was prepared from diacetyl, when it was found to coincide with our product in every respect, the yellow crystals from carbon disulfide being especially characteristic, as they consisted of rhombic plates with the acute angles truncated, and in every case one of these truncating planes was nearer the obtuse angles than the other giving the crystals the shape of a coffin. For greater certainty our product was analyzed.

Calc. for $\text{CHBr}_2\text{COCOCHBr}_2$: C, 11.94; H, 0.50; Br, 79.60. Found: C, 12.07; H, 0.85; Br, 79.68, 79.58.

Hydriodic acid produced the same substance, when 1 g. of hexabromodiacetyl previously moistened with water was shaken with 2 cc. of the constant boiling acid. After filtering out the iodine the filtrate was extracted with ether, or allowed to evaporate. The product was recognized by its melting point $94-95^{\circ}$ (uncorr.) as tetrabromodiacetyl, which is moderately soluble in water.

Pentabromodiacetylmonoethylhemiacetal, $\text{CBr}_2\text{HCOC}(\text{OHOC}_2\text{H}_5)\text{CBr}_2$.—Ten grams of hexabromodiacetyl dissolved in 150 cc. of alcohol and 15 cc. of acetone were allowed to stand 5–8 weeks at ordinary temperatures. The product, after the solvents had evaporated spontaneously, consisted of two substances, the hexabromodiacetylmonoethylhemiacetal, and another, which was distinctly more soluble in alcohol, and therefore

¹ Longer standing yielded the same product.

was washed away from the hexabrom compound with this solvent. The separation thus roughly effected was completed by crystallization from petroleum ether, in which the hexabrom compound is less soluble. In this way the constant melting point 115° (uncorr.) was at last obtained. The analyses given in the introduction show this is the *pentabromodi-acetylmonoethylhemiacetal*.

Properties.—It crystallizes from petroleum ether in short, broad prisms terminated by a second prism at right angles to the first, so that they look like somewhat lengthened octahedra. They are modified by many small planes. It melts at 115° (uncorr.); and is soluble in alcohol, methyl alcohol, benzene, tetrachloride of carbon, or glacial acetic acid; insoluble in water. Sodium hydroxide did not set free bromoform from it.

The following experiments to obtain the corresponding methyl compound gave negative results,—hexabromodiacetyl with methyl alcohol and acetone, its monomethylhemiacetal with acetone, or with methyl alcohol and acetone. The only substance isolated in each case was hexabromodiacetylmonomethylhemiacetal.

Action of Potassium Iodide on Hexabromodiacetyl.—To a solution of 3 g. of potassium iodide in 25 cc. of water was added 1 g. of powdered hexabromodiacetyl. A brown color soon appeared, which gradually grew darker, and was accompanied by the evolution of carbonic dioxide in large quantity. After 2 days a crystalline precipitate had formed, which was filtered out, washed with a solution of potassium iodide to remove the free iodine, and allowed to stand on a porous plate for 10–12 hours, at the end of which time the iodine had disappeared to judge from the color. It was not easy to find a good solvent for this substance, as most of the common ones set free iodine from it, but at last it was found that tetrachloride of carbon gave good crystals without a colored mother liquor, and accordingly it was crystallized 5 times from that, when it decomposed between 122 and 125° ; but this point varied so much with the conditions of the heating that it is of little value as a criterion of purity. We therefore analyzed specimens from the first, second, third and fourth crystallizations, and found that the impurities had been removed by the first, as the results from the last 3 (given below) agreed with each other.

Subs. 0.1468, 0.2129, 0.1366, 0.1845, 0.2439, AgBr_3AgI 0.2568, 0.3730, 0.2392, CO_2 0.0519, 0.0679, H_2O 0.0122, 0.0133. Found: BrI_2 , 90.28, 90.44, 90.40; C, 7.67, 7.59; H, 0.78, 0.61.

The formula we assign to this substance is $\text{C}_3\text{H}_2\text{BrI}_2\text{O}$ which requires BrI_2 89.52, C 6.99, H 0.39, molecular weight 515 (found 475, 485, 502). These percentages do not agree very well with those found, but this is accounted for by the fact that the only solvent which did not decompose our substance was tetrachloride of carbon, and according to our experience substances crystallized from this usually give poor results on analysis.

If this empirical formula is correct, the substance is probably triiodobromoacetone, and we have adopted this structure for it provisionally.

Properties of Triiodobromoacetone?—It crystallizes from tetrachloride of carbon in slender, lemon-yellow needles, which turn brown in the light. It melts with decomposition at $122-125^{\circ}$, but this point is decidedly indefinite. It is soluble in alcohol, methyl alcohol, benzene, chloroform, or tetrachloride of carbon; essentially insoluble in petroleum ether. All of these solvents decompose it somewhat with liberation of iodine, but this action is least with tetrachloride of carbon, which is therefore the best solvent for it. Fuming nitric in the cold or strong nitric acid when heated decomposes it, setting free iodine. Nitric acid diluted with acetic acid had no action in the cold, but on warming iodine was set free. Ammonium hydroxide gave a smell like iodoform, and ammonium iodide was found in the liquid. Sodium hydroxide also gave iodoform to judge by the smell. Hydric dioxide did not act on it.

Hexabromodiacetylmonoethylhemiacetal was not affected by potassium iodide solution even at 100° .

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

NORMAL NONANE.

BY LATHAM CLARKE AND ROGER ADAMS.

Received August 16, 1915.

Normal nonane was first synthetically produced by Krafft,¹ by reduction of pelargonic acid, $C_9H_{18}O_2$, with hydriodic acid and phosphorus in a sealed tube heated to 240° . The boiling point at 760 mm. is given by Krafft as 149.5° and the specific gravity, compared to water at 4° , is as follows: 0° , 0.7330; 13.5° , 0.7228; 15° , 0.7217; 20° , 0.7177; 99.1° , 0.6541.

We found the boiling point as $150.4-150.6^{\circ}$ at 759 mm. The specific gravity at 15° , compared to water at 15° , is 0.7219. The index of refraction, $n_D^{25} = 1.4025$.

The starting point in the preparation of normal nonane was castor oil. By distillation this yielded oenanthol (normal heptyl aldehyde), which, after purification by means of the bisulfite compound, was treated with ethyl magnesium bromide giving, after the usual decomposition of the organo-magnesium derivative, ethyl hexyl carbinol, or 3-nonanol. This carbinol was converted into the corresponding carbinol iodide by treatment with iodine and red phosphorus, and the resulting 3-iodononane was boiled with alcoholic potash, which gave nonylene. This last yielded normal nonane on reduction.

¹ Ber., 15, 1692 (1882).

Summary.

Castor oil \rightarrow

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$, oenanthol \rightarrow

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, 3-nonanol \rightarrow

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{J})\text{CH}_2\text{CH}_3$, 3-iodononane \rightarrow

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}_3 \rightarrow$

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, normal nonane.

Experimental.

Oenanthol.—The process used for obtaining oenanthol was a slight modification of the one used by Erlenmeyer.¹ Five hundred grams of castor oil were poured into a three-liter flask, which was connected to a condenser containing water in the jacket, but not running water. The flask was placed on a sand bath and strongly heated. A rather rapid distillation of liquid ensued, and the heating was continued until the flow of distillate had considerably slackened, then the burners were removed. The residue in the flask was poured out while still hot. If the heating was continued too long, the residue began to foam badly and became a sort of spongy material, exceedingly hard to remove from the flask.

The distillate was redistilled and a fraction collected between 90° and 180° . This was shaken with a concentrated solution of pure sodium bisulfite and the aldehyde-bisulfite compound crystallized out. This was filtered and pressed out on a clay plate. The best method for the resolution of this into pure normal heptyl aldehyde was to treat with an excess of saturated sodium carbonate solution and distil carefully with steam.

The aldehyde was separated from the water in the distillate, dried over calcium chloride,² and redistilled. The fraction boiling at $152-157^\circ$ was that used in subsequent work.

Ethyl-hexyl Carbinol (3-Nonanol).—A solution of ethyl magnesium bromide was prepared by dissolving 12 g. of magnesium in a mixture of 60 g. of ethyl bromide and twice its volume of absolute ether. To this, 57 g. of oenanthol in its own volume of absolute ether was gradually added, and the whole allowed to stand several hours at room temperature. The organo-magnesium compound was decomposed in the usual way with water and dilute sulfuric acid. The ether layer containing the carbinol was separated, and dried over potassium carbonate. The ether was then distilled off and the residue fractionated. 45 g. of carbinol were thus obtained, boiling at $192-193^\circ$ at 755 mm.

This alcohol has been previously made by Wagner from oenanthol and zinc ethyl,³ and by Gerard from oenanthol and ethyl magnesium bromide.⁴

¹ *Ann.*, 176, 342 (1875).

² Calcium chloride did not have any detectable chemical action on this aldehyde, and was found to be a very efficient drying agent for it.

³ *J. Russ. Chem. Soc.*, 16, 306.

⁴ *Chem. Zentr.*, 1907, I, 1398.

3-Iodononane.—This was obtained from 3-nonanol by the usual procedure for the conversion of alcohols into iodides. In a typical experiment 40 g. of 3-nonanol were mixed with 4 g. of red phosphorus and 36 g. of iodide. The mixture, which at first was artificially cooled, was later heated for two hours on the steam bath, then filtered to remove unchanged red phosphorus, washed with water to remove acids of phosphorus, and without further purification was converted into nonylene.

Normal Nonylene.—The above 3-iodononane was refluxed with excess of strong alcoholic potash for about an hour. The liquid in the reaction flask was distilled, and yielded a solution of nonylene and alcohol, these forming a mixture of minimum boiling point. On the addition of much water, the hydrocarbon separated as a floating layer, which was removed, washed with water, dried with calcium chloride and distilled from metallic sodium. On subsequent fractionation, the main portion boiled at 149.4–149.9°.

Properties.—Colorless liquid, very mobile, pleasant petroleum-like odor. It boils at 149.4–149.9° and has at 15° the specific gravity 0.7540 compared to water at 15°.

Calculated for C_9H_{18} : C, 85.7; H, 14.3. Found: C, 85.3; H, 14.2.

Normal Nonane.—Normal nonylene was reduced to normal nonane by passing the vapor of the former, together with hydrogen, over freshly reduced nickel at a temperature of 160°.¹

Properties.—Colorless, very mobile liquid, with a very slight "sweetish" odor. B. p. 150.4–150.6° at 759 mm. The specific gravity at 15° compared to water at 15° is 0.7219. The index of refraction n_D^{25} = 1.4025. It is miscible with the common organic solvents.

Calculated for C_9H_{20} : C, 84.4; H, 15.6. Found: C, 84.1; H, 15.7.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF THE NITRO- α -CARBOPYRROLIC ACIDS.²

BY WILLIAM J. HALE AND WILLIAM V. HOYT.

Received August 14, 1915.

In 1882 Weidel and Ciamician³ prepared the first nitro derivative of the pyrrole ring in the form of a nitrocarbopyrrollic acid. The dry distillation of gelatin yielded pyrocoll, and this product, upon careful nitr-

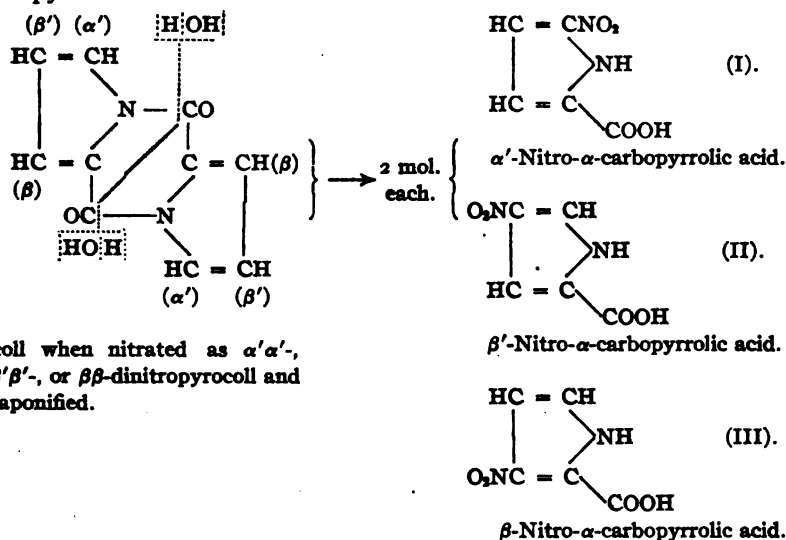
¹ The exact procedure may be found in an article by Clarke and Beggs, *THE JOURNAL*, 34, 59 (1912).

² The work described in this article forms part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan by William V. Hoyt.

³ *Gazz. chim. ital.*, 12, 39 (1882).

tion with fuming nitric acid, was converted into a dinitropyrocoll, which was in turn readily saponified by cold alkali into a nitro- α -carbopyrrollic acid (m. p. $144-6^\circ$). These investigators had previously established the constitution of pyrocoll¹ by a study of its decomposition products—its hydrolysis, for example, gave only α -carbopyrrollic acid. Later Ciamician and Silber² synthesized pyrocoll by the action of acetic anhydride upon α -carbopyrrollic acid, thus leaving no room for doubt as to the constitution of this crystalline product.

With the production of this nitro- α -carbopyrrollic acid alone, through the nitration of pyrocoll, Weidel and Ciamician correctly assumed that the nitration must have proceeded symmetrically in respect to the two pyrrole nuclei in the pyrocoll molecule. Three distinct symmetrical dinitro derivatives ($\alpha'\alpha'$ -, $\beta'\beta'$ -, $\beta\beta$ -) of pyrocoll are possible. These therefore must yield by hydrolysis three distinct (α' -, β' - and β -) nitro- α -carbopyrrollic acids as here shown.



Pyrocoll when nitrated as $\alpha'\alpha'$ -, $\beta'\beta'$ -, or $\beta\beta$ -dinitropyrocoll and saponified.

Although Ciamician and Silber had succeeded in obtaining only this one nitro- α -carbopyrrollic acid melting at 146° , they made many attempts to prepare the other two isomers. Their attempts, however, resulted in failures.³ They found, for example, that the action of nitric acid upon α -carbopyrrollic acid led to decomposition into dinitropyrroles and carbon dioxide. Anderlini,⁴ on the other hand, was able to introduce the nitro group into the methyl ester of α -carbopyrrollic acid without this

¹ *Monats.*, 1, 281 (1880).

² *Ber.*, 17, 103 (1884).

³ *Ibid.*, 19, 1080 (1886).

⁴ *Gazz. chim. ital.*, 19, 93 (1889).

chance for decomposition. The methyl ester was slowly added to concentrated nitric acid cooled with ice. The dark brown solution was then poured into cold water and the solution made almost neutral with sodium hydroxide, after which it was made slightly alkaline with sodium carbonate and extracted with ether. From the ether extract Anderlini obtained the yellow methyl ester of a mononitro- α -carbopyrrolic acid and again, by the hydrolysis of this ester, he obtained a pale yellow acid crystallizing with one molecule of water of crystallization, as was noted also for the acid melting at 146° . This new acid, when anhydrous, melted at 217° .

In the same year Anderlini¹ was able to isolate the third isomeric nitro- α -carbopyrrolic acid from the mother liquors left upon removal of the ester of the acid melting at 217° . These liquors, already alkaline with sodium carbonate, were acidified and again extracted with ether. From the ether extract a mixture of nitro compounds was obtained, but by fractional crystallization from water a new methyl ester was isolated and, by hydrolysis, was found to give the third nitro- α -carbopyrrolic acid expected. This acid also contained one molecule of water of crystallization but when anhydrous (after standing over sulfuric acid) melted at 161° . The nitration of the methyl ester therefore led to the production of the two previously unknown nitro- α -carbopyrrolic acids. Though all three nitro derivatives may have been present in the nitration product of the ester, Anderlini was unable to isolate the ester of the first known nitro acid of Ciamician (m. p. 146°).

With the three nitro- α -carbopyrrolic acids thus known and obtainable only in minutest quantity, little evidence could be advanced concerning their exact structures. The fact that the ester of the acid melting at 217° could be removed from an alkaline solution by extraction with ether evidenced its lack of any acid properties and led Anderlini to suppose that the nitro group occupied most probably one of the β -positions, a position farthest removed from the imino hydrogen atom.

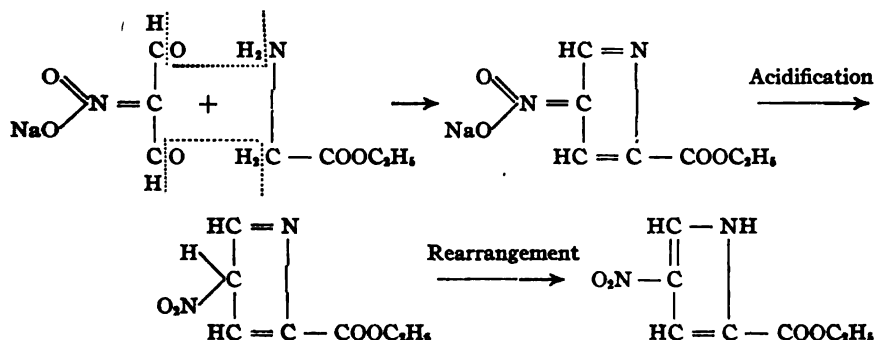
The study of condensation involving certain dialdehydes—especially that of nitromalonic aldehyde, has led to interesting syntheses of many well-known ring structures. In the use of nitromalonic aldehyde the fixed position of the nitro group upon the middle carbon atom has sufficed for the determination of the constitution of certain hitherto unknown nitro derivatives. Thus the condensation of urea with this aldehyde led to the synthesis of 5-nitropyrimidines.² And in the same manner as amino groups, so also methylene groups are found to condense more or less readily with this dialdehyde.³ It occurred to us, therefore, that a

¹ *Gazz. chim. ital.*, 19, 350 (1889).

² *THIS JOURNAL*, 34, 82 (1912).

³ *Ber.*, 45, 1596 (1912).

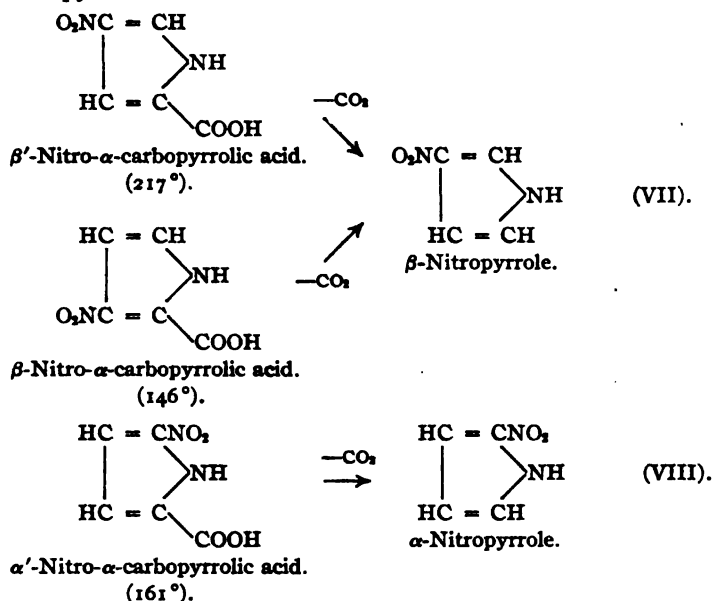
simple condensation of nitromalonic aldehyde with amino acetic acid might be expected to yield a pyrrole-carboxylic acid. The presence of an acid is not, however, advantageous for a great majority of such condensations, consequently the ester of amino acetic acid, glycine ester, was selected for the condensation thus to be made in neutral or alkaline solution. The reactions involved may here be shown.



The result of this condensation will be seen at once to give an ethyl ester of a nitro pyrrole-carboxylic acid, namely, the ester of β' -nitro- α -carbopyrrolic acid—one of the three nitro acids under discussion. This possible identification of one of the much-discussed acids with an acid synthesized by simple means, and concerning the constitution of which there can be no room for doubt, offered us the hope that the means before us might lead to establishing the constitution of the other two acids.

When, however, glycine ester hydrochloride and sodium nitromalonic aldehyde were brought together in dilute alcoholic solution, there soon separated from the mixture a slightly soluble yellow compound which was still aldehydic in character and possessed no ring structure (IV). The compound proved to be of an intermediate type, the amino group having first entered into condensation with one aldehyde group, as was evidenced by failure of tests to confirm the presence of either a primary or a secondary amine. The possibility of further condensation between the remaining aldehyde group and the methylene group was not eliminated and reactions to this purpose were found to be easily accomplished in the presence of alkaline condensing agents. In the previous case it was advantageous to add a few drops of sodium hydroxide solution; the alkali facilitated the condensation and yet at the same time was too dilute to form a sodium salt with the almost insoluble acid product precipitated. In order to effect the latter step the reaction mixture was made strongly alkaline with sodium hydroxide and warmed upon the water bath. The intermediate product, β,β -aldehydonitro-ethyliden-aminoacetic ester (IV), is easily soluble in an excess of alkali and from the

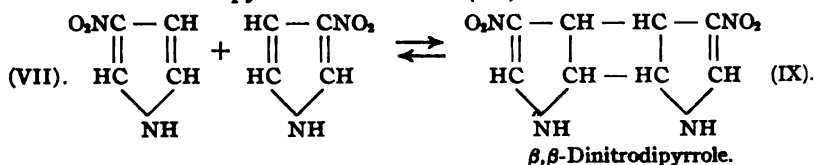
carboxylic acids we chose to determine which one of these two might be made to yield the same decomposition product as that of the 217° acid upon the loss of carbon dioxide. No further reactions of substitution were planned, and hence by loss of carbon dioxide we should arrive at a simple nitropyrrole. It was known that free carbopyrrolic acids readily evolved carbon dioxide upon heating. Each of the three nitrocarbopyrrolic acids therefore should yield a nitropyrrole but, as will be seen below, the acid with the constitution determined by us must yield the same β -nitropyrrole as one of the other two. In other words, there is no need but to study the decomposition of one of the two remaining nitrocarbopyrrolic acids in order to fix the constitution of all three.



The proof of these three structures seemed almost in hand, when it was found that but one nitropyrrole had been prepared and nothing definite was known regarding its constitution. This nitropyrrole in question had been prepared by Angeli and Alessandri¹ by the nitration of pyrrole with ethyl nitrate in the presence of sodium alcoholate. Their method will be described later. Their conclusions seemed to point to the β -position for the nitro group, though their argument was altogether from analogy: α -methyl indole yielded a β -nitroso derivative whereas β -methyl indole gave no similar derivative, hence it is to be supposed that nitration in the pyrrole ring selects the beta position. The nitropyrrole prepared by these investigators was a yellow, crystalline product melting at 63.5°. If Angeli and Alessandri were correct in their deductions

¹ *Atti dei Lincei* [1] 20, 311 (1911).

then we should be able to obtain the same β -nitropyrrole by the action of heat upon our acid of known constitution (m. p. 217°). Numerous attempts to drive off carbon dioxide from this acid met with failure. Upon heating it alone, violent decomposition always ensued. The use of equal quantities of naphthalene, however, sufficed for its successful decomposition, when the two substances were heated together in a sealed tube. From the decomposition products thus finally obtained we have been able to isolate a small amount of a substance melting at 63.5° and in every way identical with the nitropyrrole described by Angeli and Alessandri. The constitution therefore of our acid (m. p. 217°) sufficed in its decomposition for the determination of the structure for nitropyrrole and checked the work of Angeli and Alessandri in selecting the β -position for the nitro group in this final product. There was obtained, however, in this same decomposition mixture as removed from the sealed tube, a new substance melting at 101° and possessing the same empirical formula as nitropyrrole— $C_4H_4O_2N_2$. The molecular weight of the compound, as determined by an elevation of the boiling point of its solution in benzene, corresponded to $C_8H_8O_4N_4$. A further determination of molecular weight by lowering of the freezing point of its aqueous solution indicated a much lower value approaching the value corresponding to a simple nitropyrrole. We may assume, therefore, that β -nitropyrrole polymerizes at higher temperatures and that in aqueous solution we have the conditions favorable for an equilibrium between the two forms. In fact, by repeated crystallization from ice cold water, we have been able to convert the 101° product into the 63.5° product. The structure of the dimolecular nitropyrrole is shown in (IX).



The formation of the dinitrodipyrrole is analogous to the formation of tripyrrole (pyrrole red) but the presence of the nitro group is naturally sufficient to stop the polymerization at the dimolecular stage.

The lower melting nitropyrrole (63.5°) has been found by us to be present only to a small extent. We could not isolate a sufficient product for a molecular-weight determination. The monomolecular product as prepared by us and also as prepared by us in accordance with the method of Angeli and Alessandri, melted accurately at 63.5° , but when heated for several minutes, not to exceed $75\text{--}80^\circ$ in the same melting point tube, the melting point at once arose to the neighborhood of 100° . In fact this change of the lower melting product to the 101° melting product seems entirely to have escaped the notice of Angeli and Alessandri.

The dimolecular form of β -nitropyrrole is thus seen to be more stable than the monomolecular form. These facts do not interfere with our conclusion that β' -nitro- α -carbopyrrolic acid by decomposition loses carbon dioxide and yields β -nitropyrrole (VII).

Naturally the next step must involve a similar decomposition for each of the two remaining nitrocarbopyrrolic acids. The acid melting at 146° , as obtained by Ciamician, was now prepared and mixed with naphthalene and heated in a sealed tube to the point of charring. From the decomposition mixture in the sealed tube we were able to isolate the same nitropyrrole (IX) melting at 101° (as well as a portion of the monomolecular form) that resulted from the decomposition of the acid melting at 217° . We must conclude, therefore, that the acid (of Ciamician) melting at 146° is no other than the β -nitro- α -carbopyrrolic acid (III).

The third acid, melting at 161° , was finally prepared according to the method of Anderlini, and in better yields by a method described in the Experimental Part. When heated with naphthalene in a sealed tube this acid underwent decomposition only slowly. Prolonged action, however, gave eventually a decomposition product which by extraction with water yielded only a very small quantity of a yellow oil. This oil was not stable and could not be obtained sufficiently pure for analysis. There can be no doubt but what this oil is α -nitropyrrole (VIII) which is to be expected from the third possible acid. The proof then of the structure of this acid (I) as an α' -nitro- α -carbopyrrolic acid is established. The instability of α -nitropyrrole is to be expected from its analogy to α -nitrothiophene and α -nitrofurfurane, both of which so far have not been prepared.

Experimental Part.

The preparation of glycine ester was accomplished by the well-known method of Emil Fischer,¹ the hydrolysis of gelatin by the action of hydrochloric acid and the final separation of the ester in the form of its hydrochloride from an absolute alcoholic solution. The preparation of sodium nitromalonic aldehyde was carried out in the usual way, by the action of sodium nitrite upon mucobromic acid.²

β,β -Aldehydonitroethylidenaminoacetic Ethyl Ester, $C_7H_{10}O_5N_2$ (IV).—Equimolecular quantities of sodium nitromalonic aldehyde (1.6 grams) and of glycine ethyl ester hydrochloride (1.4 grams) were dissolved in 6–7 cc. of 60–70% alcohol, and the mixture gently warmed for a few minutes upon the water bath to effect complete solution. When this was accomplished the reaction mixture was allowed to stand at room temperature, whereupon, in the course of 15–30 minutes, the yellow product

¹ *Z. physiol. Chem.*, **33**, 151 (1901); see Fischer's "Untersuchungen über amino-säuren," p. 672 (1906).

² *Am. Chem. J.*, **22**, 25 (1899).

crystallized out. Calculated upon the basis of the sodium nitromalonic aldehyde the yield of the crude product came to 80% of the theoretical yield of ethylidenaminoacetic ester. This ester is readily soluble in acetone, chloroform, ethyl acetate or acetic acid; fairly soluble in alcohol, ether, water or benzene, crystallizing well from each; slightly soluble in carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It crystallizes best from alcohol or water in the form of thin, pale yellow prisms melting at 104° . Hofmann's carbylamine test when applied to this ester failed to show the presence of the original primary amine group. The presence of a secondary amine also could not be detected, whereas the action of this ester in the presence of an ammoniacal solution of silver nitrate showed the presence still of an aldehyde group, a point further established by the formation of a crystalline phenylhydrazone by the action of phenylhydrazine. The compound, therefore, may be considered as of the structure previously described. This intermediate product is very stable toward acid solutions, crystallizing well from concentrated hydrochloric acid. Alkalies transform it into the pyrrole derivative, but when in extreme dilution they are comparatively without action upon it. In view of this the first step in the condensation between the glycine ester and nitromalonic aldehyde may often be hastened by the addition of only a few drops of sodium hydroxide solution.

0.1702 g. subst. gave 0.2582 g. CO_2 and 0.0791 g. H_2O ; 0.1452 g. subst. gave 18.6 cc. N_2 (24° and 745.4 mm. over H_2O).

Calc. for $\text{C}_7\text{H}_{10}\text{O}_4\text{N}_2$: C, 41.57; H, 4.98; N, 13.87. Found: C, 41.37; H, 5.19; N, 14.01.

β' -Nitro- α -carbopyrrolic Ethyl Ester, $\text{C}_7\text{H}_8\text{O}_4\text{N}_2$ (VI).—When 1 g. of β, β -aldehydonitroethylidenaminoacetic ethyl ester, dissolved in 8 cc. of 65% alcohol and treated with 40 drops of a 20% sodium hydroxide solution, was warmed on the water bath at a temperature not above 50° , red crystals of β' -nitro- α -carbopyrrolic ester separated from the red reaction mixture in the course of half an hour. Tarry substances were inclined to form when the temperature overstepped 50° . The yield of the product amounted to about 90% of the theoretical nitrocarbopyrrolic ester calculated from the weight of ethylidenaminoacetic ester taken.

The preparation of this intermediate ethylidenaminoacetic ester is in no wise necessary, as the condensation may be carried through in one process. Equimolecular quantities of sodium nitromalonic aldehyde (1.6 g.) and of glycine ethyl ester hydrochloride (1.4 g.) were dissolved in 6–7 cc. of warm 65% alcohol. 40 drops of a 20% sodium hydroxide solution were then added and the red reaction mixture set aside for half an hour at a constant temperature of 50° . At the end of this time the red crystalline mass which had separated was removed, washed with alcohol and dried. The yield amounted to 75% of the theoretical nitrocarbo-

pyrrolic acid ester when based upon the aldehyde salt employed. The pure product is readily soluble in acetone or acetic acid; fairly soluble in alcohol, ether, benzene, chloroform, or ethyl acetate; slightly soluble in water, carbon tetrachloride, or carbon disulfide, and insoluble in ligroin. It is best purified by crystallization from alcohol, from which it separates in almost colorless, glistening prisms melting at 174° .

0.1736 g. subst. gave 0.2896 g. CO_2 and 0.0702 g. H_2O ; 0.1823 g. subst. gave 25.3 cc. N_2 (23.2° and 748.2 mm. over H_2O).

Calc. for $\text{C}_7\text{H}_6\text{O}_4\text{N}_2$: C, 45.63%; H, 4.39; N, 15.23. Found: C, 45.50; H, 4.52; N, 15.31.

β' -Nitro- α -carbopyrrolic Methyl Ester, $\text{C}_6\text{H}_6\text{O}_4\text{N}_2$.—This product was prepared in an identical manner to that of the preceding ethyl ester, glycine methyl ester replacing the previously employed glycine ethyl ester. The pure substance is readily soluble in acetone; fairly soluble in alcohol, ether, benzene, ethyl acetate, chloroform or acetic acid, crystallizing well from each; slightly soluble in water, carbon disulfide, or carbon tetrachloride, and insoluble in ligroin. It crystallizes best from alcohol in almost colorless prisms melting at 198° . This product was prepared primarily to check that product which had been reported by Anderlini¹ as melting at 197° . The two products were found to be identical in all respects and when mixed melted practically at 198° .

0.1581 g. subst. gave 0.2448 g. CO_2 and 0.0538 g. H_2O .

Calc. for $\text{C}_6\text{H}_6\text{O}_4\text{N}_2$: C, 42.35%; H, 3.54%. Found: C, 42.22; H, 3.81.

β' -Nitro- α -carbopyrrolic Acid, $\text{C}_6\text{H}_4\text{O}_5\text{N}_2$ (II).—One gram of β' -nitro- α -carbopyrrolic ethyl ester was brought into solution with 15 cc. of a 20% potassium hydroxide solution and the contents of the flask warmed for 5–6 hours under a reflux condenser upon a steam bath. The yellow solution was then cooled by placing the flask in a freezing mixture and concentrated hydrochloric acid added to the point of neutralization, whereupon the yellow color disappeared. Without especial cooling the heat of neutralization would lead to decomposition of the acid sought. The neutral solution was next extracted with ether and a pale yellow product thus removed. The yield amounted to 90% of the theoretical weight of the acid. This free acid is readily soluble in alcohol, ether, ethyl acetate, or acetone; fairly soluble in water or glacial acetic acid; slightly soluble in chloroform, benzene, carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It crystallizes well from hot water in beautiful, colorless needles which melt with decomposition at 217° . It crystallizes unchanged from glacial acetic acid. Anderlini obtained this same acid by the hydrolysis of the nitro- α -carbopyrrolic methyl ester previously described. The acid which he obtained was, of course, the same as is obtained by the hydrolysis of the ethyl ester. Our product melting at 217° ,

¹ *Loc. cit.*

when mixed with his, melted constant at the same point and in all respects the two acids were found to be identical. They each contain one molecule of water of crystallization which is readily lost by standing in a desiccator over sulfuric acid.

0.5033 g. subst. lost 0.0508 g. H_2O over H_2SO_4 in 48 hours.

Calc. for $C_6H_4O_4N_2 \cdot H_2O$: H_2O , 10.33%. Found: H_2O , 10.09%.

0.2106 g. anhydrous subst. gave 0.2974 g. CO_2 and 0.0495 g. H_2O ; 0.1341 g. anhydrous subst. gave 21.9 cc. N_2 (21° and 745.5 mm. over H_2O).

Calc. for $C_6H_4O_4N_2$: C, 38.47; H, 2.56; N, 17.96. Found: C, 38.52; H, 2.63; N, 18.14.

By the action of potassium carbonate this acid was converted into the corresponding potassium salt, which is extremely soluble in water but crystallizes from its concentrated solution in the form of needles or prisms of a light yellow color.

0.1814 g. K salt gave 0.0827 g. K_2SO_4 .

Calc. for $C_6H_3O_4N_2K$: K, 20.17%. Found: K, 20.47.

The salt therefore contains no water of crystallization.

The silver salt of this acid is easily precipitated by the addition of a silver nitrate solution to an aqueous solution of the acid made neutral with ammonium hydroxide. It forms a yellow, flocculent, precipitate.

0.2885 g. subst. gave 0.2064 g. $AgBr$.

Calc. for $C_6H_3O_4N_2Ag$: Ag, 41.04%. Found: Ag, 41.09.

β -Nitro- α -carbopyrrolic Acid, $C_6H_4O_2N_2$ (III).—This acid, the first known of the nitrocarbopyrrolic series, was prepared by Ciamician¹ from pyrocoll by the action of fuming nitric acid. Our method differed but slightly from his and required a definite strength of nitric acid and the maintenance of a constant temperature. Two grams of pyrocoll were added in small portions to about 40 g. of nitric acid (sp. gr. = 1.50) cooled to $4-10^\circ$. When all of the pyrocoll had been added, the red solution was warmed upon the steam bath for a few moments and then poured into an excess of ice-water. The dark yellow, noncrystalline precipitate of a dinitropyrocoll was filtered off and treated at once with 20 cc. of a 20% sodium hydroxide solution. The mixture was then heated upon the steam bath until a test portion failed to give a precipitate when acidified with dilute sulfuric acid. When this hydrolysis was thus shown to be complete the solution was cooled by a freezing mixture and finally acidified by dilute sulfuric acid. Extraction with ether removed the yellow, crystalline product melting at $140-6^\circ$ as obtained by Ciamician. This β -nitro- α -carbopyrrolic acid is readily soluble in acetone, alcohol, ether, ethyl acetate or acetic acid; fairly soluble in chloroform, benzene or water; slightly soluble in carbon disulfide or carbon tetrachloride and insoluble in ligroin. β' -Nitro- α -carbopyrrolic acid is somewhat more

¹ *Loc. cit.*

soluble in water than this acid, whereas α' -nitro- α -carbopyrrolic acid is somewhat less soluble in water. The acid crystallizes best from water in almost colorless needles containing one molecule of water of crystallization. The anhydrous acid melts at 146° .

β -Nitro- α -carbopyrrolic Methyl Ester, $C_6H_8O_4N_2$.—Although the three nitro- α -carbopyrrolic acids have been known, only two of the corresponding esters are described in the literature. The methyl ester of β' -nitro- α -carbopyrrolic acid, melting at 198° , and the methyl ester of α' -nitro- α -carbopyrrolic acid, melting at 179° . As the third, β -nitro- α -carbopyrrolic acid was readily converted into its methyl ester by an hour's heating of the silver salt with methyl iodide under a reflux condenser. The ether extract of the dry residual mass gave the crude ester. This methyl ester is readily soluble in acetone; fairly soluble in alcohol, ether, benzene, ethyl acetate, chloroform or acetic acid, crystallizing best from alcohol; slightly soluble in water and insoluble in ligroin. The pure ester melted at 162° .

α' -Nitro- α -carbopyrrolic Acid, $C_6H_8O_4N_2$ (I).—This acid can be prepared by the method of Anderlini¹ in which α -carbopyrrolic ester is nitrated directly with nitric acid. The yield is exceedingly small and no appreciable amount can be prepared by this process. We have studied the reaction under a wide range of temperature and concentrations of acid and find it in no way practicable. The α -carbopyrrolic ester here employed may best be prepared by the method of Oddo,² which far surpasses the other methods that may be mentioned. But even with a good method for the production of the ester the next step, namely its nitration, failed to give satisfactory results. There is no doubt but what all three nitrocarbopyrrolic acids are to be found in the reaction mixture. For these reasons we have chosen preferably to work with the residues left upon the nitration of pyrocoll according to the method of Ciamician. By certain nitrations of pyrocoll, namely those carried out at lower temperatures, we were able to procure an appreciable quantity of this α' -nitro- α -carbopyrrolic acid sufficient for the purpose of this investigation. In a subsequent communication we shall describe the methods in detail. The pure α' -nitro- α -carbopyrrolic acid as obtained by us from pyrocoll, as well as by the method of Anderlini, is readily soluble in acetic acid, acetone, alcohol, ether or ethyl acetate; fairly soluble in chloroform, benzene, or water, crystallizing from either in small, colorless, needle clusters; slightly soluble in carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It is best purified by crystallization from water from which it separates with one molecule of water of crystallization. The anhydrous acid melts sharply at 161° .

¹ *Loc. cit.*

² *Gazz. chim. ital.*, [1] 39, 649 (1909).

Decomposition of the Nitro- α -carbopyrrolic Acids into the Corresponding Nitropyrroles.—The decomposition of the carbopyrrolic acids by heat alone is well known. Attempts, however, to decompose these three nitrocarbopyrrolic acids met with many failures. Heating the acids alone resulted in explosive decompositions. When the β' -nitro- α -carbopyrrolic acid, m. p. 217° , and of which we possessed a good supply, was heated with pumice, lime, soda-lime, sand, finely divided copper, nickel, and other metals, no satisfactory product could be procured. A distillation of the acid under diminished pressure, however, gave us a very small quantity of a nitropyrrole, but far better results were obtained when equal quantities of this acid and naphthalene were heated in a sealed tube up to, but not beyond, the point of slight charring, when the heating was discontinued. By the action of hot water upon this reaction mixture we were able to extract a fair quantity of a dark yellow crystalline product of no definite melting point. When the product was digested for a few minutes with ice water we obtained a yellow solution which, upon spontaneous evaporation, yielded small prisms of nitropyrrole melting at 63.5° . The part left undissolved by the ice-water was now dissolved in warm water and this solution also allowed to evaporate spontaneously. From this portion we obtained small, yellow prisms melting, when pure, at 101° . It was next observed that the nitropyrrole melting at 63.5° underwent some change when warmed for any length of time at 70 – 80° . The product resulting was found to have a melting point at 101° . This led us at once to the belief that the higher melting substance was a polymer of the first product. A molecular-weight determination confirmed this view, as will be seen in the discussion of these two nitropyrroles under the next heading.

The preparation of a nitropyrrole by the elimination of carbon dioxide from our β' -nitro- α -carbopyrrolic acid indicates directly the constitution of the nitropyrrole produced, namely that of a β -nitropyrrole. This, as will be seen shortly, is identical with the nitropyrrole obtained by Angeli and Alessandri.¹

The method just described for the elimination of carbon dioxide from β' -nitro- α -carbopyrrolic acid with consequent production of nitropyrrole, was next applied to the β -nitro- α -carbopyrrolic acid, melting at 145° . Under exactly analogous conditions we were able to reproduce the same results as described with β' -nitro- α -carbopyrrolic acid. The β -nitropyrrole obtained was in every way identical with that previously described. The conclusion is, therefore, evident: these two acids which give the same β -nitropyrrole must have the nitro groups in the β' - and β -positions, respectively.

When the third acid, α' -nitro- α -carbopyrrolic acid, was subjected to

¹ *Loc. cit.*

this same decomposition reaction with naphthalene in a sealed tube, the product yielded no trace of a β -nitropyrrole but only a yellow, oily substance of no definite stability. We identified it as a nitro product and one which could not be purified. We may, therefore, conclude that it is the α -nitropyrrole which evidently would be formed by the elimination of carbon dioxide from the acid in question.

Monomolecular β -Nitropyrrole, $C_4H_4O_2N_2$.—In order to check conclusively our results with those of Angeli and Alessandri,¹ who first prepared a nitropyrrole, we have reproduced their results as follows: 5 g. of pyrrole were dissolved in 30–40 cc. of dry ether and to this solution 2.4 g. of sodium wire and 9.51 g. of ethyl nitrate were added. The flask with its contents was now warmed under a reflux condenser protected from the air by a U-tube containing strong alkali. The temperature, however, was not permitted to rise over 30°. Into this flask, after about 48 hours, when the sodium had completely dissolved and a dark brown salt had separated out, small pieces of ice were added and the mixture extracted with ether to remove any pyrrole unacted upon. The cold aqueous residue was then treated with bone-black and the clear filtrate treated with a silver nitrate solution, whereupon a dark yellow, non-crystalline precipitate was formed. This latter step must be carried out in the absence of all but a ruby light. Though no mention is made of this fact by the authors, we have found it absolutely essential to the success of the experiment. The precipitate was filtered off and washed repeatedly with cold water until no appreciable amount of silver remained in the washings. While still moist this precipitate was treated with sodium chloride and water. Silver chloride and the excess of sodium chloride were removed by filtration. The clear, yellow solution was now saturated with carbon dioxide and extracted with ether, from which by evaporation a yellow oil was obtained. At this stage we found that it was advantageous to dissolve the oil in a mixture of benzene and high-boiling ligroin and after treating with bone-black to allow the solution to evaporate in the open air. When cooled the residual oil slowly gives small yellow highly refractive crystals of nitropyrrole. These melted at 63.5° as described by the authors. Upon heating for a short time it was observed that this product had slowly changed into that higher melting substance (101°) which we obtained in the decomposition of two of the nitro-carbopyrrollic acids. The yield of β -nitropyrrole from the method just described cannot much exceed 1% of the theoretical quantity, but for our purpose we were able to secure sufficient to confirm the identity of the products from these two sources mentioned. The decomposition of β' -nitro- α -carbopyrrollic acid gave us the best yield in β -nitropyrrole—approximately 50% of the theoretical value.

¹ *Loc. cit.*

β,β -Dinitrodipyrrole, $C_8H_8O_4N_4$ (IX).—This substance, which we have shown to be readily prepared by heating the monomolecular form for a few minutes at a point slightly above its melting point, 63.5° , is best purified by crystallization from water in pale yellow prisms melting at 101° . It may also be crystallized from benzene in the form of yellow plates. It is readily soluble in alcohol, acetone, ethyl acetate, or acetic acid; fairly soluble in water, benzene, or chloroform, and almost insoluble in ligroin, carbon tetrachloride or carbon disulfide.

0.1437 g. subst. gave 0.2270 g. CO_2 and 0.0493 g. H_2O ; 0.1216 g. subst. gave 27.6 cc. N_2 (21.1° and 743.0 mm. over H_2O).

Calc. for $(C_4H_4O_2N_2)_2$: C, 42.85; H, 3.59; N, 25.01. Found: C, 43.08; H, 3.84; N, 25.12.

Subst. 0.1294 g., 0.2694 g., 0.4222 g.; benzene, 15.2 g.; elevation, 0.097, 0.200, 0.401.

Calc. for $(C_4H_4O_2N_2)_2$: 224.06. Found: 222.0.

Subst. 0.0981 g.; water, 32.32 g.; depression, 0.035.

Calc. for $(C_4H_4O_2N_2)_2$: 224.06. Found: 161.3.

Although the product maintains its dimolecular structure at higher temperatures and in anhydrous solvents, the action of cold water alone is seemingly sufficient for a partial dissociation into the monomolecular form as just indicated. The preparation of β -nitropyrrole cannot be successfully accomplished by the method of Angeli and Alessandri. Though the method we have described for its preparation gives fair yields any large quantity must be found difficult to prepare.

Summary.

1. Pyrrole- α -carboxylic acid (α -carbopyrrolic acid) had been known to yield three distinct nitro derivatives. The position of the nitro group, however, in any one of these acids could not be determined.

2. The synthesis of β' -nitro- α -carbopyrrolic acid from nitromalonic aldehyde and glycine ester lead to the identity of one of these three unknown nitro acids.

3. With one acid thus known the decomposition of each was studied. Heating with naphthalene in sealed tubes sufficed for the elimination of carbon dioxide from each and for the consequent production of a nitropyrrole as residue. The β' -nitro- α -carbopyrrolic acid gave β -nitropyrrole as expected. The other nitro acid, therefore, which yielded the same β -nitropyrrole became identified at once as β -nitro- α -carbopyrrolic acid, whereas that acid which yielded the unstable α -nitropyrrole was necessarily accorded the constitution of an α' -nitro- α -carbopyrrolic acid.

4. Although the constitution of nitropyrrole itself had previously been unknown, the work here described establishes it as a β -nitropyrrole, a compound readily transformed into a dimolecular form β,β -dinitrodipyrrole. The unstable α -nitropyrrole was found incapable of isolation.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MONTANA.]

SOME SALTS OF THE HALOGENOACETIC ACIDS. II.

BY W. G. BATEMAN AND D. B. CONRAD.

Received August 16, 1915.

In an earlier paper¹ some salts of monochloro- and trichloroacetic acids were described. This article discusses some more compounds formed by these acids and in addition derivatives of dichloroacetic and monobromoacetic acids.

$\text{CHCl}_2\text{CO}_2\text{NH}_4$.—Ammonium dichloroacetate was prepared by passing dry ammonia into an absolute ether solution of dichloroacetic acid. The white precipitate which formed was filtered off and washed free from the acid with ether. Keiser and McMaster² first used this method for the preparation of neutral ammonium salts of organic acids and later McMaster³ amplified the method and described many compounds prepared in this way. Among the solvents which may be used are alcohol, ether and acetone. We have found where the acids are fairly strong, as in the cases of dichloro- and trichloroacetic acids, that a solvent other than alcohol should be used. Both these acids formed with absolute alcohol a fair quantity of ethyl ester, the amount being increased if the solution became hot while ammonia was being absorbed. Under these conditions no precipitate was obtained. Upon evaporation of the alcohol a syrup-like liquid results, which is a solution of the ammonium salt in the ester, and from which the dry salt is obtained with some trouble. If the original solution is distilled, alcohol is first obtained, then the ester and a residue of the salt is left behind. In ether or acetone solutions these difficulties are not encountered, and not in alcohol if the acid be weak.

When prepared as above, ammonium dichloroacetate forms in white leaflets very lustrous and pearly. It is not deliquescent, has a slight halogen odor and is quite stable. When dissolved in water, in which it is very soluble, it gives first a neutral solution, but this soon becomes acid due to hydrolysis. This salt is very soluble in ethyl alcohol, another reason for not preparing it in this liquid. It dissolves readily in ethyl acetate, acetone, ethyl dichloroacetate, methyl alcohol and acetate, but not in ether or benzene and only slightly in ethyl butyrate and iso-amylbenzoate.

When heated carefully the compound volatilizes in white fumes having an odor of ammonia. Upon stronger heating it chars, while dichloroacetic acid, ammonia and carbon dioxide are evolved.

¹ Bateman and Hoel, *THIS JOURNAL*, **36**, 2517 (1914).

² Keiser and McMaster, *Am. Chem. J.*, **49**, 84 (1913).

³ McMaster, *Ibid.*, **49**, 294 (1913); *THIS JOURNAL*, **36**, 742 and 1916 (1914).

drous salt. This is less soluble in water than the hydrate and also less soluble in absolute alcohol, with which it forms a green solution.

When a dilute solution of phenylhydrazine in absolute alcohol is added to a solution in the same reagent of the copper salt of any one of the chloroacetic acids, olive-colored substances precipitate at once. These are no doubt addition products such as phenylhydrazine forms so readily. They promptly decompose, however, with vigorous evolution of nitrogen. Next a white precipitate settles out in long needles. This is quite unstable, for when exposed to the air it turns copper-red in color, the same effect being brought about by water, only more energetically. These precipitates dissolve readily in ammonium hydroxide, but at first give colorless solutions which upon shaking with air become green and finally the deep familiar blue. Hydrochloric acid solutions quickly become colored brown.

If phenylhydrazine is used to excess and if the mixture be allowed to become hot, cuprous oxide is formed and in some cases what appeared to be free copper. Sometimes the odor of benzene is perceived.

The white precipitate is chiefly cuprous chloride, which is changed by the action of moist air or water into cuprous oxide as stated by Lescœur¹ and Haywood.² It may contain, however, the salt of phenylhydrazine and the chloroacetic acid whose copper salt is used.

Still other substances are sometimes found. If the alcohol solution from the reacting mixture is diluted with water a white crystalline substance separates. This is diphenylamine, or some substitution product, since it has the agreeable odor and gives the usual test with nitric acid characteristic of this compound. Tafel,³ and later Gatterman, Johnson and Hölzle,⁴ found diphenylamine derivatives to be formed by reducing phenylhydrazines with copper acetate and decomposing the resulting compounds.

If the solution is hot and oxidation energetic, the ethyl ester of the acid is sometimes recognized by its odor. When copper monochloroacetate is concerned, the reaction mixture usually has a strong, aromatic, spicy odor. This is no doubt due to monochloroacetaldehyde, since Tafel⁵ found aldehyde to be formed with copper acetate. This is all the more probable since, when copper trichloroacetate is used, the familiar, sweet, pungent odor of chloral can at times be detected. Monochloroacetaldehyde is said to have a powerful odor.

Finally chlorobenzene is formed. Gattermann and Hölzle⁶ have

¹ Lescœur, *Ann. chim. phys.*, 7, 97 (1894).

² Haywood, *J. Phys. Chem.*, 1, 411 (1897).

³ Tafel, *Ber.*, 25, 413 (1892).

⁴ Gatterman, Johnson and Hölzle, *Ibid.*, 25, 1075 (1892).

⁵ Tafel, *Ibid.*, 25, 413 (1892).

⁶ Gatterman and Hölzle, *Ibid.*, 25, 1074 (1892).

shown that the monohalogen benzene compounds can be prepared by the action of copper sulfate on phenylhydrazine in the presence of hydrogen halides with the separation of cuprous chloride or metallic copper.

Comparison of Copper Acetate with the Copper Chloroacetates.

Color.— $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ has a deep green color.

$\text{Cu}(\text{CH}_2\text{ClCO}_2)_2 \cdot 4\text{H}_2\text{O}$ has the same green color but lighter in shade.

$\text{Cu}(\text{CHCl}_2\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ is deep blue in color.

$\text{Cu}(\text{CCl}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ is medium blue in color.

The anhydrous chloro salts all have a bright blue-green color, but $\text{Cu}(\text{CHCl}_2\text{CO}_2)_2$ is paler than the rest, while anhydrous copper acetate is white.

Solubility.—The salts of the substituted acids are more soluble, in general, than copper acetate. This is especially so with ethyl acetate, in which copper acetate dissolves only slightly, while the copper chloroacetates are very soluble. Copper halides are soluble as observed by Naumann.¹

Stability and Reactivity.—Copper acetate is more stable than the copper chloro-salts but the latter are more active, especially in oxidation reactions.

$\text{Cu}(\text{CH}_2\text{BrCO}_2)_2 \cdot \text{H}_2\text{O}$.—This copper salt was prepared in the same way as the others. It crystallizes from deep green solutions in masses of small, dark green crystals similar in appearance to those of copper acetate itself and hence darker in color than those of copper chloroacetate. It is very soluble in water, alcohol, acetone and ethyl acetate, and somewhat soluble in ether and glacial acetic acid. It is insoluble in benzene.

Copper monobromoacetate reacts with phenylhydrazine in a manner analogous to the action of the chloro-salts, but slower and less vigorous. Cuprous bromide is formed which reacts with moist air or water to give metallic copper and cuprous oxide, but this action is weaker than with cuprous chloride.²

Calc. for $\text{Cu}(\text{CH}_2\text{BrCO}_2)_2 \cdot \text{H}_2\text{O}$: Cu, 17.78; H_2O , 5.03. Found: Cu, 17.69; H_2O , 5.14.

$\text{Cu}(\text{CH}_2\text{BrCO}_2)_2$.—The anhydrous salt has a blue-green color and is soluble in the same reagents as the hydrate, but in somewhat less degree.

If a solution of copper bromoacetate is heated for a time on the steam bath, it becomes brown in color and copper bromide separates from the cooled solution. This salt, then, is more susceptible to hydrolysis than copper chloroacetate.

$\text{Hg}(\text{CH}_2\text{ClCO}_2)_2$.—Mercury monochloroacetate was prepared by add-

¹ Naumann, *Ber.*, 43, 314 (1910).

² Bödlander and Storbeck, *Z. anorg. Chem.*, 31, 1 and 458 (1902).

ing in small quantities at a time pure mercuric oxide to a hot water solution of the acid. The latter was kept always in excess. After a time, a white precipitate separated in shining leaflets from the hot solution. This was filtered off and the cool solutions left to crystallize. From them a white, coarsely crystalline substance was obtained having a slight tinge of yellow. Both forms are, however, the anhydrous salt.

Calc. for $\text{Hg}(\text{CH}_2\text{ClCO}_2)_2$: Hg, 52.44. Found: leaflets, Hg, 52.54;¹ crystals, 52.50.

This compound is only sparingly soluble in water, alcohol, acetone and ethyl acetate. When hydrogen sulfide is passed through the solution in ethyl acetate a bright orange precipitate is first formed but this quickly becomes black.² If dry ammonia be passed into the solution in the same solvent the salt is reduced with the formation of mercury. Other mercuric salts form ammonates.³

When mercuric monochloroacetate is heated, it begins to melt at 135° and boils at 140° . While boiling it becomes slightly pink in color. At 150° boiling ceases and the temperature rises to 185° before further action takes place. Then the residue rapidly becomes black and at 190° is mostly free mercury.

When this salt is treated with ammonium hydroxide a fine, white powder is precipitated which becomes yellow in color upon sparing washing and drying. This, if only ammonolysis⁴ takes place, would be $\text{NH}_4\text{HgCH}_2\text{ClCO}_2$ with a mercury content of 64%. If both ammonolysis and hydrolysis take place we might expect the monochloroacetate of Milon's base since, as shown by Franklin, salts of this base are usually found where ammonium hydroxide reacts with mercuric salts. The above compound contains 76% mercury. Analysis of the sample, however, gave values in the neighborhood of 85%. HOHgNH_2 requires about this quantity of mercury, but 2% nitrogen, while our preparation contained only 0.25% of the latter.

$\text{Hg}(\text{CCl}_3\text{CO}_2)_2$.—We tried to prepare this salt by the action of the acid on mercuric oxide since this plan succeeded with the monochloro salt. However, it did not work well in this case. Water solutions of the acid will keep on reacting with mercuric oxide long after the theoretical quantity has been used. White, amorphous substances separate out, containing varying amounts of mercury, and the solution gives forth a variety of sweet odors. If mercuric oxide in the right quantity is added, little by little, to a water solution of the acid, a beautiful, white, crystalline mass of shining needles soon collects on the top of the liquid. This apparently

¹ This analysis was kindly made for us by Mr. A. B. Hoel.

² Neumann, *Ber.*, 43, 313 (1910).

³ Neumann, *Loc. cit.*; Franklin, *THIS JOURNAL*, 29, 35 (1907).

⁴ Franklin, *Loc. cit.*

is the mercuric compound, but we never succeeded in getting it pure. Almost at once it falls to the bottom of the dish in the form of a white powder and this, when examined and analyzed, proves to be almost pure mercurous chloride.

Calc. for Hg_2Cl_2 : Hg, 84.95. Found: 84.57.

Other attempts gave mixtures of mercurous and mercuric salts and basic salts. According to Beilstein, Clermont¹ prepared this salt in prismatic needles, but we have not seen the original paper.

$\text{Hg}_2(\text{CCl}_3\text{CO}_2)_2$.—This salt was prepared by adding a solution of trichloroacetic acid to a freshly prepared solution of mercurous nitrate. A snow-white precipitate consisting of small needles was thrown down. If this is allowed to crystallize from water, in which it is but sparingly soluble, it can be obtained in large beautiful needles.

Calc. for $\text{Hg}_2(\text{CCl}_3\text{CO}_2)_2$: Hg, 55.19. Found: 55.39.

While sparingly soluble in water, this substance is very soluble in alcohol, ethyl acetate, acetone, benzene and toluene, and somewhat so in ether. If dry hydrogen sulfide be passed through the solution in benzene a precipitate consisting of mercuric sulfide and mercury is produced. Ammonium hydroxide immediately decomposes mercurous trichloroacetate. Toward heating it is very stable and volatilizes at temperatures over 200° with very little decomposition.

$\text{Hg}_2(\text{CH}_2\text{ClCO}_2)_2$.—The mercurous salt was prepared by pouring a solution of the acid into a freshly prepared solution of mercurous nitrate containing enough nitric acid to prevent hydrolysis. A snow-white precipitate fell down which, when dry, consisted of a fluffy mass of small needles.

Calc. for $\text{Hg}_2(\text{CH}_2\text{ClCO}_2)_2$: Hg, 68.12. Found: 68.36.

This salt is but slightly soluble in water and insoluble in alcohol, ether, ethyl acetate and acetone. When treated with ammonium hydroxide it is completely decomposed in a manner analogous to other mercurous salts. When heated in the presence of water vapor it is quite unstable and darkens readily. If heated dry it does not change much below 180° , at which point it melts with some decomposition, a white powder subliming in the tube and a black residue being left.

$\text{Hg}_2(\text{CH}_2\text{BrCO}_2)_2$.—Mercurous monobromoacetate was prepared in the same way as the other mercurous salts. It is an amorphous, white powder only slightly soluble in water. In alcohol, ether, acetone, ethyl acetate and benzene it is insoluble. When heated it begins to darken at 145° , becomes yellow—due to liberated bromine—and sublimes without melting. The usual behavior of mercurous compounds with ammonia is shown by this salt.

Calc. for $\text{Hg}_2(\text{CH}_2\text{BrCO}_2)_2$: Hg, 59.18. Found: 59.42.

¹ *Jahrsb. fort. Chem.*, 1871, 550.

When solutions of mercurous nitrate and dichloroacetic acid are brought together no precipitation occurs; even after standing, no salt of the organic acid separates. This mercurous salt then, if formed, is an exception to its class in being apparently so soluble.

The same difficulty was met when the mercuric salt of dichloroacetic acid was sought by bringing the acid and mercuric oxide together as in the case of trichloroacetic acid. The compound obtained was always a mixture of mercurous and mercuric salts. The dichloro acid is, however, more stable in this respect than its trichloro relative.

Summary.

1. In the two papers of this series the preparation, analysis, description and properties of about twenty-five salts of monochloro, dichloro, trichloro and monobromo acetic acids are discussed. No, or very scanty, information concerning these appears to be in the literature.

2. The action of the copper salts of the above acids on phenylhydrazine is found to be complex, strong reduction taking place with the formation of cuprous halides, phenylhydrazine salts of the halogeno acids, cuprous salts of the same, diphenylamine derivatives, chlorobenzene and other products depending upon conditions.

3. The series of copper chloroacetates is compared with copper acetates.

4. Some of the mercury salts of the above acids are found interesting. Mercurous dichloroacetate appears to be very soluble in water while mercurous trichloroacetate is very soluble in all the ordinary organic solvents.

5. A number of reactions of some of these salts in such nonaqueous solvents as ethyl acetate and benzene are described.

MISSOULA, MONTANA.

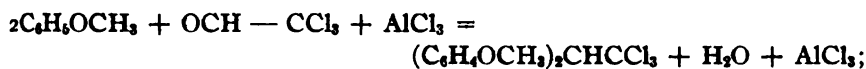
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA] THE ACTION OF ALUMINIUM CHLORIDE ON THE ALIPHATIC ETHERS.

BY G. B. FRANKFORTER AND E. A. DANIELS.

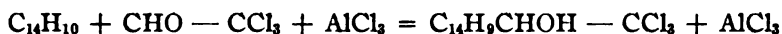
Received August 27, 1915.

It has been shown by Frankforter and Kritchevsky¹ that aluminium chloride not only acts as a catalyst according to the well-known Friedel-Crafts reaction, but also as a dehydrating reagent, removing a molecule of water according to the common condensation reaction. In some cases, however, they found that it gave the aldol reaction when the ketone aldehydes, namely chloral and bromal, were brought in contact with other reacting constituents. Thus, when methyl phenyl ether is treated with chloral in the presence of aluminium chloride, the following aldol quantitative reaction takes place if the temperature is kept low enough.

¹ *Bull.* 2, Chemical Studies, University of Minnesota.



but, when anthracene is treated with chloral in the presence of aluminium chloride, the aldol reaction takes place according to the following equation:



In a very few cases aluminium chloride was found to combine directly with the reacting components forming unstable compounds.

Following out the line of work mentioned above as well as the work of Frankforter and Poppe,¹ the aliphatic ethers were treated with chloral in the presence of aluminium chloride and finally with the chloride alone. It was soon found that the reaction with the aliphatic ethers does not proceed along the same lines as observed in the aromatic ethers. However, the reaction proved to be of considerable interest, although it was extremely complex.

The first experiments were tried with common ethyl ether and chloral in the presence of aluminium chloride. Although the conditions were widely varied, the reaction seemed extremely complex in each case and no compounds analogous to those obtained from the aromatic ethers were formed, but when commercial ether was used, a heavy, white, flocculent precipitate was formed. The formation of this precipitate which was subsequently found to be due to moisture in the ether was used as a basis for a qualitative test for water in ether.

It was thought that the complex reaction was due, partly at least, to reactions between two of the constituents, namely, aluminium chloride and chloral, or aluminium chloride and ether. Thus Combes² found that chloral and aluminium chloride react on each other, forming tetrachlorethylene and a polymerized form of chloral which he called perchloral. We were unable to obtain this compound. In fact, we were unable to identify any of the compounds formed in this experiment.

The experiments which follow were carried out with perfectly dry ether, inasmuch as we found that water in the ether completely changed the reaction. In order to eliminate any possibility of moisture during the reaction, a flask was fitted with a two-hole stopper, one hole connected with a calcium chloride drying tube and the other carrying a thermometer in order to observe the temperature. The mixture of ether and chloral was placed in the flask and cooled down to 0°, then powdered aluminium chloride was added in 5 g. portions. A large amount of heat was generated notwithstanding the fact that the flask was kept in ice-water. At the same time a small amount of hydrochloric acid was liberated and

¹ *8th Intern. Congr. Appl. Chem.*, 25, 363 (1910).

² *Ann. Chem.*, [6] 12, 3, 199 (1887).

escaped through the drying tube. Aluminium chloride was added until the ether was saturated and a small quantity of solid chloride was left in the bottom of the flask. We were unable to prove that the hydrochloric acid gas liberated was not due to the action of moisture on the chloride.

It required about an hour to add the chloride. At the end of that time the solution had changed from a perfectly colorless to a straw yellow. After standing in ice-water for two hours, the flask was removed and the temperature allowed to slowly rise to room temperature. The color changed with the rise in temperature until at 22° it was a reddish brown. The mixture was then allowed to stand over night at a temperature of 0° . In the morning the whole mass had changed to a light brown jelly. It turned darker on standing at room temperature. Treated with water a large amount of heat was liberated and the substance separated out as a thick, dark brown mass. This was subjected to steam distillation when several substances were obtained, but the quantities were too small to permit a careful examination. During the distillation, there was distinct odor of ether. The viscous insoluble material remaining in the flask after the steam distillation was filtered off and examined. It was dissolved in ether and filtered. There remained an undissolved gelatinous substance which subsequently was found to be a simple aluminium compound.

The ether extract, which carried practically all of the organic substance left upon evaporation a dark brown resinous mass. It was distilled under diminished pressure. At 52° and 22 mm. pressure, crystals formed in the condenser, evidently chloral hydrate; at $62-80^{\circ}$ and the same pressure, a small amount of liquid passed over, then the temperature rapidly rose to 125° , when a very small quantity of a liquid passed over, but the quantity was too small for exhaustive examination. The residue left in the flask was of a dark brown color and appeared charred. With the hope of obtaining more satisfactory results, the above experiment was repeated, except that the temperature was kept at -8° instead of 0° . The same reaction seemed to take place although the results obtained by steam distillation *in vacuo* were somewhat different. A small quantity of liquid passed over at 100° , together with a large amount of hydrochloric acid. The oil was found to react vigorously with water, and is evidently an organic compound of aluminium chloride. Crystals passed off between 110 and 135° . They were removed, pressed between filter paper and finally dried in a desiccator over sulfuric acid. They melted at $22-24^{\circ}$ and readily decomposed in the air, changing to a liquid. The quantity of substance, however, was not sufficient for an exhaustive examination. They were doubtless the compound of aluminium chloride and ether to be described later. The residue left in the flask was insoluble in ether.

It was partially soluble in water with evolution of heat and a peculiar disagreeable odor. An exhaustive examination of the residue failed to yield a definite compound.

The Action of Aluminium Chloride on Ether.—It was observed early in the above experiments that aluminium chloride combined readily with ether, producing a well crystallized compound. Absolute ether was therefore treated with equal weight of anhydrous aluminium chloride at a low temperature. The solution immediately changed to a dark purple and much heat was liberated. The mixture was kept at -15° over night. In the morning the whole was a solid mass of well defined crystals. These crystals were found to dissolve when the room temperature was reached, but reformed on cooling. They were found to react violently with water.

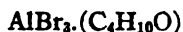
In going over the literature it was found that various salts of ether had been prepared. Thus titanium chloride¹ was found to combine with ether and to form a double salt. Tin, bismuth, zinc, arsenic and antimony chlorides and bromides² form double salts with ether, representing the general formula,



Boeseken,³ in his work on aluminium chloride, prepared an acetyl double salt by treating acetyl chloride dissolved in carbon disulfide with aluminium chloride, to which he gave the formula



Plotnikov⁴ described a double salt of ether and aluminium bromide to which he gave the formula



and Walker and Spencer⁵ in a study of the action of aluminium chloride on organic compounds containing oxygen incidentally studied the reaction between ethyl ether and aluminium chloride. They dissolved the organic substance in carbon disulfide and then added the aluminium chloride. Evaporating off the solvent by a current of dry air, they obtained large brown plates. They obtained by analysis 13.93% of Al for the compound to which they ascribed the formula



The theoretical for Al is 13.01%.

Inasmuch as the reaction between ether and aluminium chloride, and especially the compound mentioned above, has not been carefully studied,

¹ *Bull. soc. chim.*, 33, 566 (1880).

² *J. Pharm.*, [3] 26, 161 and *J. prakt. chem.*, 83, 259 (1861).

³ *Rec. trav. chim.*, 20, 102 (1901).

⁴ *Z. anorg. Chem.*, 56, 53 (1907).

⁵ *J. Chem. Soc.*, 85, 1106 (1904).

escaped through the drying tube. Aluminium chloride was added, the ether was saturated and a small quantity of solid chloride was in the bottom of the flask. We were unable to prove that the chloric acid gas liberated was not due to the action of moisture on the chloride.

It required about an hour to add the chloride. At the end of this time the solution had changed from a perfectly colorless to a straw color. After standing in ice-water for two hours, the flask was removed and the temperature allowed to slowly rise to room temperature. The color changed with the rise in temperature until at 22° it was a red. The mixture was then allowed to stand over night at a temperature of 0°. In the morning the whole mass had changed to a light red. It turned darker on standing at room temperature. Treatment with a large amount of heat was liberated and the substance appeared as a thick, dark brown mass. This was subjected to steam distillation when several substances were obtained, but the quantities were too small to permit a careful examination. During the distillation a distinct odor of ether. The viscous insoluble material was removed from the flask after the steam distillation was filtered off and extracted with ether, dissolved in ether and filtered. There remained an undissolved substance which subsequently was found to be a simple solid.

The ether extract, which carried practically all of the volatile material, left upon evaporation a dark brown resinous mass which was removed under diminished pressure. At 52° and 22 mm. pressure, in the condenser, evidently chloral hydrate; at 62-80° and 22 mm. pressure, a small amount of liquid passed over, then the temperature rose to 125°, when a very small quantity of a liquid passed over, the quantity was too small for exhaustive examination. The flask was of a dark brown color and appeared to be empty. In hope of obtaining more satisfactory results, the distillation was repeated, except that the temperature was kept at 100°. The same reaction seemed to take place although the distillation *in vacuo* were somewhat different. A small amount of liquid passed over at 100°, together with a large amount of solid. The oil was found to react vigorously with water. The solid was a organic compound of aluminium chloride. Crystals were obtained at 110 and 135°. They were removed, pressed between filter papers and dried in a desiccator over sulfuric acid. They readily decomposed in the air, changing to a dark brown substance, however, was not sufficient for analysis. They were doubtless the compound of aluminium and chlorine to be described later. The residue left in the flask

ACTION OF ALUMINIUM CHLORIDE ON ALIPHATIC ETHERS. 2563

as partially soluble in water with evolution of heat and a peculiar agreeable odor. An exhaustive examination of the residue failed to give a definite compound.

Action of Aluminium Chloride on Ether.—It was observed early in the above experiments that aluminium chloride combined readily with ether, producing a well crystallized compound. Absolute ether was treated with equal weight of anhydrous aluminium chloride at room temperature. The solution immediately changed to a dark color and much heat was liberated. The mixture was kept at -15° . In the morning the whole was a solid mass of well defined crystals. These crystals were found to dissolve when the room temperature was reached, but reformed on cooling. They were found to react with water.

From the literature it was found that various salts of ether were prepared. Thus titanium chloride was found to combine with ether to form a double salt. Tin, bismuth, zinc, arsenic, antimony, and bromine form double salts with ether, the general formula being $\text{SnCl}_4 \cdot 2\text{C}_2\text{H}_5\text{O}$ and $\text{SbBr}_3 \cdot 2\text{C}_2\text{H}_5\text{O}$.

Work on aluminium chloride with ether was continued. It was found that aluminium chloride combined with ether to form a double salt. The general formula for this double salt is $\text{AlCl}_3 \cdot 2\text{C}_2\text{H}_5\text{O}$.

This double salt is a white crystalline solid, soluble in ether and alcohol. It is stable in the dry state but decomposes on heating.

The decomposition of the double salt was studied. It was found that the double salt decomposes into aluminium chloride and ether at 100° . The reaction is reversible, and the double salt can be reformed by treating the products with ether.

The reaction of aluminium chloride with ether is of interest in connection with the study of the catalytic action of aluminium chloride in the Friedel-Crafts reaction. It is found that the double salt acts as a catalyst in the reaction of benzene with acetyl chloride.

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detection of water in ether, and that the test which we propose is by far the most delicate, convenient, and practical of any now in use.

The procedure found to be best is given below. Five to ten cubic centimeters of the ether to be tested are placed in a dry test tube and the tube closed with a rubber stopper. This is then cooled to about 10° by ice or running water, a piece of fresh anhydrous aluminium chloride of the size of a kernel of wheat dropped in, the tube again stoppered and observed with a black background. As the ether warms to room temperature, a reaction takes place, evidenced by the formation of small bubbles which rise to the top of the liquid carrying with them, in the presence of water, a delicate white cloud which, if present in large enough amount, will spread out as a milky layer near the top of the ether.

The density of the cloud, of course, depends upon the amount of water present. If there is an appreciable amount present, the precipitate remains permanent on shaking. This cloud, if present in small amount, is soluble or coagulated if too much aluminium chloride is present, if the solution is agitated, and thirdly, if the reaction is allowed to proceed at too rapid a rate.

The test is rendered obscure by the presence of alcohol in comparatively large amounts; thus, 7% of absolute alcohol will cover up the tests entirely, while 5% does not. Alcohol present in ether in this amount can readily be detected by the hydrogen evolved upon the addition of metallic sodium. Moisture of the air does not affect it, as the exposure to air is very short. Ether, direct from chemical houses, in every case shows a positive test. Ether dried over calcium chloride always gives a positive test. Ether which had been allowed to stand over metallic sodium, refluxed and distilled until moisture was proven absent by the above test, was placed in a glass stoppered bottle which was opened only occasionally and allowed to stand for several weeks. It gave at the end of this time a positive test. This proves that anhydrous ether like practically every other absolutely dry substance is hygroscopic.

The test is intended to prove the complete dehydration of ether by sodium and has been found delicate enough to detect one drop of water in 500 cc. of ether which had been freshly distilled over sodium.

Conclusions.

1. No definite products could be isolated from the reaction between chloral and ether in the presence of aluminium chloride.
2. The compound, $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_4\text{H}_{10}\text{O}$, an addition product of ethyl ether and aluminium chloride, has been prepared and its physical and chemical properties studied.
3. The addition product of aluminium chloride and normal propyl ether, analogous to the ethyl ether compound, has been prepared and described for the first time.

4. A new qualitative test for water in ether has been proposed and is thought to be very satisfactory and quickly made.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA.]

VERATRINE AND SOME OF ITS DERIVATIVES. II.

BY GEO. B. FRANKFORTER AND W. KRITCHEVSKY.

Received August 23, 1915.

The alkaloid known as veratrine, or cevadine, as it has recently been named, has been studied by one of us several years ago.¹ A number of derivatives were studied in order to determine the constitution of the alkaloid.

Among other derivatives, a chloralhydro-veratrine was prepared from chloral and veratrine. As chloral and veratrine are of great importance physiologically, it was thought that a condensation product of the two substances might be interesting pharmacologically. We therefore decided to take up the study of that compound again in order to determine the true nature of the chemical reaction between the two substances. It was obvious that if the reaction is a true condensation reaction, the new compound formed would possess properties entirely different from either of the components. It would therefore quite likely have different physiological properties. If, on the contrary, the substance proved to be an additive product, then its physiological properties would be the result of one or both of the reacting constituents.

Compounds of cevadine and cevine with chloral and bromal were therefore prepared by the following general method:

The alkaloid was dissolved in carbon disulfide and the necessary amount of chloral added. A precipitate formed at once and the reacting mixture became warm. After the reaction had ceased and the solution cooled to room temperature, cold ether was added and the precipitate filtered off. It was washed with ether several times, dried and analyzed. Neither the analysis nor the molecular weight determination proves conclusively that the new compound formed was either a condensation or an additive product. When heated in a drying oven at a temperature of 130–140° for several hours it was found that the compounds lost weight and did not contain either chlorine or bromine. A qualitative study proved that the loss was equal to the percentage of the aldehyde originally present. This shows conclusively that the new compounds are simple additive products. We have not been able to find any definite ratio between the chloral and the alkaloid. We found that by varying the conditions, namely, the quantity of aldehyde, we were able to change the ratio between the reacting components which enter the new molecule.

¹ *Am. Chem. J.*, 20, 358.

On the other hand, we found that the halogen aldehydes combine with practically all of the alkaloids soluble in carbon disulfide, forming additive products insoluble in ether. This reaction may be used, therefore, as a class reaction for alkaloids.

Experimental Part.

Cevadine-Chloral, $2C_{22}H_{49}NO_9.CCl_3CHO$.—One part of cevadine was dissolved in ten of carbon disulfide and one part of chloral added. Very little heat was formed. The reaction seemed to be complete in half an hour. Ether was added, when a white, amorphous substance was precipitated. It was washed several times with ether and dried; m. p. 220° .

Calc. for $2C_{22}H_{49}NO_9.CCl_3CHO$: Cl, 7.98; N, 2.11. Found Cl, 8.12; N, 2.32.

The substance was dried at a temperature of $130-140^\circ$, until the constant weight was reached. The loss amounts to 10.88% of the original weight of the substance. The percentage of chloral in the substance is 11.06%. The remaining resinous substance shows all the properties of cevadine. A quantitative determination failed to give an appreciable amount of chlorine.

Cevadine-Chloral, $2C_{22}H_{49}NO_9.3CCl_3CHO$.—One part of cevadine was dissolved in five of carbon disulfide and 10 parts of chloral added. A white precipitate was formed at once. It was filtered, washed with ether in order to remove the excess of chloral, and dried; m. p. 209° .

Calc. for $2C_{22}H_{49}NO_9.3CCl_3CHO$: Cl, 19.59; N, 1.73. Found: Cl, 19.50; N, 1.85.
Loss on drying at $130-140^\circ$, 26.95; chloral, 27.20.

Cevine-Chloral, $C_{27}H_{48}NO_8.CCl_3CHO$.—One part of cevine was dissolved in five of carbon disulfide and 25 parts of chloral added. The white precipitate formed was filtered, washed with ether to remove the excess of chloral, and dried; m. p. $206-208^\circ$. Analyses gave the following:

Calc. for $C_{27}H_{48}NO_8.3CCl_3CHO$: Cl, 33.47; N, 1.47. Found: Cl, 33.68; N, 1.66.
Loss on drying at $130-140^\circ$, 46.30; chloral, 46.41.

Cevadine-Bromal, $2C_{22}H_{49}NO_9.CBr_3CHO$.—One part of cevadine was dissolved in ten of carbon disulfide and five molecules of bromal added. The precipitate formed in the process was filtered, washed with ether and dried. The precipitate was a bright yellow powder with a m. p. of 162° .

Calc. for $2C_{22}H_{49}NO_9.CBr_3CHO$: Br, 16.30; N, 1.91. Found: Br, 16.50; N, 2.07.
Loss on drying, 19.29; bromal, 19.58.

Cevine-Bromal, $2C_{27}H_{48}NO_8.CBr_3CHO$.—One molecule of cevine was dissolved in ten volumes of carbon disulfide and five molecules of bromal added. The precipitate was filtered, washed and dried. The substance is a bright yellow powder with a m. p. 106° .

Calc. for $C_{27}H_{48}NO_8.CBr_3CHO$: Br, 18.47; N, 2.16. Found: Br, 18.21; N, 2.29.
Loss on drying, 21.45; bromal, 21.63.

The action of chloral on alkaloids in general.—When an alkaloid is dissolved in carbon disulfide and chloral or bromal added to it, a precipitate is formed which is insoluble in ether. This is true of every alkaloid soluble in carbon disulfide which we have studied. The powder formed is an additive compound of the alkaloid and the aldehyde.

The following alkaloids were studied: Cevadine, cevine, nicotine, codeine, brucine, strychnine, cocaine, conine, chinchonine and papaverine. In every case the precipitate formed was insoluble in ether.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

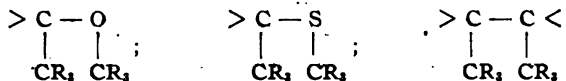
TRIPHENYLMETHYL. XXIV. THE ADDITIVE COMPOUNDS OF TRIPHENYLMETHYL AND SOME SATURATED HYDROCARBONS.

BY M. GOMBERG AND C. S. SCHORFFLE.

Received August 26, 1915.

The unsaturated character of triphenylmethyl is strikingly illustrated by its tendency to unite spontaneously with compounds of various types. In fact, it is rather difficult to find solvents from which triphenylmethyl crystallizes without taking up solvent of crystallization. Triphenylmethyl has been found to unite in this manner with ethers, esters, ketones, aldehydes, and nitriles; with olefines and with aromatic hydrocarbons; with carbon disulfide, with chloroform, etc.¹

The trivalency of carbon in triphenylmethyl is sufficient in itself to account for the additive tendencies of the free radical. On the other hand, it seems rather difficult to find a plausible explanation in terms of graphic formulas for the additive compounds thus produced. In the esters, ketones, and aldehydes, we have the double linking C = O; in carbon disulfide, the corresponding C = S; while in the aromatic hydrocarbons and in the olefines, we have the grouping C = C. But it seems hardly probable that in all these instances triphenylmethyl adds itself in virtue of the double bond in the various compounds. If this were the case, we should expect the addition to result in fairly stable substances, as for example, in the addition of the Grignard reagent to aldehydes, ketones, esters, etc.

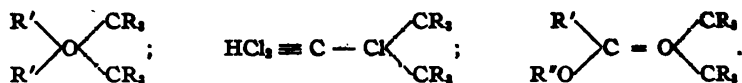


But as a matter of fact, the addition compounds in the triphenylmethyl series are extremely unstable, dissociating readily at temperatures of 50–100°, into the original components. Indeed, the stability of these additive compounds is apparently no greater than that of the additive com-

¹ THIS JOURNAL, 36, 1147 (1914).

binations that result from triphenylmethyl with ethylene oxide, with ethers, with chloroform, all of which contain no double bond of any kind whatsoever.

An explanation in terms of the valence hypothesis for the existence of all the various additive compounds might still be had, if we are willing to assume that the oxygen, the sulfur, or the chlorine atom, as the case may be, functions as having acquired a higher valence state than it ordinarily possesses. Sulfur and chlorine are known, of course, to be endowed with the capacity of variable valence, and of late, although the proof is far from satisfactory, it has become customary to consider that oxygen, too, can acquire a higher than its usual valence state.



While such an explanation might perhaps account for the addition of triphenylmethyl to ethers, esters, etc.,¹ the question still remains unanswered as to the mechanism of the addition of the free radical to the olefines.

The problem of finding a satisfactory explanation in terms of the valence hypothesis that would account for the existence and the nature of all of these additive compounds becomes still more puzzling when we take into consideration the rather unusual circumstance that triphenylmethyl unites with completely saturated hydrocarbons. In a previous paper² it has been shown that such additive compounds are probably formed. But since the hydrocarbons employed in those experiments consisted merely of purified samples of petroleum ethers, the alternative was not entirely excluded, that these hydrocarbons might have still retained a small amount of some member of the olefine series. Because of the theoretical interest attached to this phase of the unsaturated character of triphenylmethyl, we have repeated the experiments, employing this time individual paraffins of natural origin which were most carefully purified and fractionated, and also some synthetic aliphatic and alicyclic hydrocarbons.

The Hydrocarbons.—The hexane and heptane used were pure products obtained from petroleum, obtained from a well-known firm. They were further purified by shaking with concentrated sulfuric acid for ten hours, with concentrated nitric acid for ten hours, and with alkaline permanganate for six hours, after which they were dried and fractionated. The octane (normal) and the decane (di-isoamyl) were synthetic products, but nonetheless, these were also shaken with concentrated sulfuric acid before fractionation. The cyclohexane and methylcyclohexane were carefully distilled before using. After this treatment, all the hydrocarbons were

¹ THIS JOURNAL, 23, 501 (1901).

² Ber., 38, 1338 (1905).

ioned above were found to be free from olefines or other similar reducing constituents.

The Additive Compounds.—The triphenylmethyl was prepared for these experiments by the action of metallic mercury upon triphenylchloromethane, with the addition of a small amount of powdered lead, which greatly facilitates the settling of the finely divided mercurous chloride formed during the reaction. Ten grams of the chloride, 10 g. of mercury, and about 0.5 g. of lead powder are placed in a small Drexel bottle, and enough dry benzene, about 75 cc., is added to almost fill the bottle. The stopper is removed and the bottle is provided with a well fitting cork; covered with parchment paper in such a manner that none of the paper projects beyond the neck of the flask. After several hours' shaking, the reaction is complete. The mercury is now allowed to settle, the cork removed, and there is rapidly inserted the glass connection which permits the syphoning off of the clear liquid into the apparatus, which has been described in a previous paper.¹ The benzene is distilled under reduced pressure, and the product recrystallized from hot acetone. The solvent is drawn off and the beautifully crystalline triphenylmethyl is washed, and then dried in a stream of carbon dioxide and finally in vacuum, the crystals remaining all the while in the same apparatus.

The triphenylmethyl prepared in the above manner was converted into the various additive compounds as follows: About 60 cc. of the saturated hydrocarbon intended for combination were added and heated as high as its boiling point would permit. The hot solution was then filtered off from the undissolved triphenylmethyl into a second similar piece of apparatus. On cooling, the additive compound separated usually in almost colorless crystals. The mother liquid was drawn off and the crystals were dried in a stream of carbon dioxide, and finally in vacuum. In the case of the higher boiling hydrocarbon decane, the crystals before being dried were freed from the adhering mother liquid by washing with a small amount of low boiling petroleum ether. It may be said that the solubility of triphenylmethyl in the fatty hydrocarbons is but slight at room temperature, decreasing, apparently, with the increase of the molecular weight of the hydrocarbon; on the other hand, the solubility shows a marked increase with the rise of temperature of the solvent. In the alicyclic hydrocarbons triphenylmethyl is more soluble, especially when the solvent is hot.

Dissociation of the Additive Compounds.—A sample of the additive derivative was weighed out in a porcelain boat, placed into a glass tube about 15 inches long and heated in an air bath at 80–110° for one to one and a half hours, a slow stream of dry carbon dioxide being passed at the same time through the tube. In the case of the additive derivatives with

¹ *Ber.*, 37, 2034 (1904).

hydrocarbons possessing a high boiling point, the tube was also connected with a suction pump, in order to facilitate the vaporization of the hydrocarbon. The loss in weight of the original sample represented in each case the amount of the hydrocarbon in combination with triphenylmethyl. The escaping vapors were condensed in a small test tube surrounded by a freezing mixture, and the distillate was examined for its identity with the solvent originally used by determining its boiling point and molecular weight, the Schleiermacher and the Bleier and Kohn methods, respectively, being employed for that purpose. The residue in the boat was identified as unchanged triphenylmethyl by conversion into the characteristic peroxide.

TABLE I.

Solvent.	Wt. of additive compd.	Loss on heating.	Loss as per cent.			Boiling points ¹ (uncorrected).		Molecular wts.	
			Found.	Calc. for (R ₃ C) ₃ X.	Calc. for R ₃ C.X.	Distillate.	Original solvent.	Found for dist.	Calc. for orig. solvent.
Hexane.....	0.8044	0.0006	0.1	15.0	26.1	...	(66-68)	...	86.1
	0.7262	0.0022	0.3
	0.9327	0.0011	0.1
Heptane.....	2.2246	0.0259	1.2	17.1	29.2	...	(94-96)	...	100.1
	2.4126	0.0101	0.4
	1.7153	0.2534	14.8
	2.7338	0.4244	15.5	95	...	96.6	...
	1.9181	0.2844	14.8	93	...	97.4	...
	3.1208	0.4558	14.6
Octane.....	1.5881	0.2288	14.4
	2.1688	0.0409	1.9	19.0	32.0	...	(122-124)	...	114.1
	1.2609	0.0185	1.5
	3.0028	0.2768	9.2	113	...	114.2	...
	2.1992	0.0140	0.6
	1.8966	0.0672	3.5	119
Decane.....	3.3074	0.1842	5.6	120	...	114.5	...
	0.8626	0.0090	1.0	22.6	36.9	...	(154-157)	...	142.2
	0.8252	0.0131	1.6	154
	1.6046	0.0095	0.6
	2.6980	0.7500	27.8	153	...	141.9	...
Cyclohexane	4.1539	1.2310	29.6	153	...	142.1	...
	2.0309	0.7029	34.6	154	...	144.3	...
	85.4	...
	5.6579	0.8362	14.8	14.7	25.7	76.5	(79-79.5)	83.7	84.1
Methyl cyclohexane.....	77	84.6	...
	4.6414	0.7343	15.8	16.8	28.7	97.5	(99-101)	98.2	98.1
	4.7550	0.7200	15.1	98	98	97.9	...

¹ The figures in parentheses indicate the range of temperature at which the whole of the liquid distilled. The figures not in parentheses were obtained by the Schleiermacher method, and consequently indicate the boiling point of the lowest fraction in the sample.

It was also found that the condensed distillate, at times, reduced a solution of potassium permanganate, but only in those cases when the heating of the additive compound was carried out at 100° or above, and for a considerable length of time. Undoubtedly, this reduction is due to some product resulting from a slight decomposition of the triphenylmethyl itself. Moreover, the amount of the reducing substance present was always slight, and seldom constituted more than about 1% of the total distillate, this being determined by comparison with samples of the original solvent, to which a definite amount of hexylene had been added. In order to make still more certain that the formation of the additive compound is not due to the presence of a small amount of an unsaturated hydrocarbon in the solvents used, we have in a few instances crystallized triphenylmethyl from the solvent in question, and then used the *filtrate* for a second and a third crystallization of fresh samples of triphenylmethyl. But the additive compounds in all such instances proved to be identical.

A summary of the results obtained is given in Table I.

Discussion of the Results.

From the results given in the table it appears that the formation of an additive compound is conditioned upon several factors. The foremost factor is, undoubtedly, the temperature at which the compound dissociates into its components; the second, the relative solubility of triphenylmethyl in the hydrocarbon in question. The higher the temperature of dissociation, the more likely will triphenylmethyl crystallize out on cooling its solution as an additive compound. On the other hand, the less is the solubility of triphenylmethyl in the particular hydrocarbon, the more apt it is to commence to crystallize while the solution is still quite hot. The result under these circumstances is quite likely to be unchanged triphenylmethyl, unless perchance the solution, ere crystallization sets in, should become supercooled, at least slightly below the dissociation temperature of the presumptive additive compound. If the latter conditions prevail, the additive compound will be formed.

Thus, with hexane, the product did not crystallize out until the solution had cooled to nearly room temperature; but the dissociation temperature is evidently still lower, so that no additive compound resulted. Likewise, with heptane, in the first two experiments cited, the product crystallized out while the solution was still quite warm, and there was no additive compound present. But in the other five experiments with the same solvent, crystallization did not occur until the solution had cooled considerably, and the product consisted almost wholly of the additive derivative. With octane, due to the decreased solubility of triphenylmethyl in it, the product invariably commenced separating while the solution was very hot, and we did not succeed in inducing supercooling. In

consequence thereof, the product that crystallized out consisted either wholly of unchanged triphenylmethyl or of triphenylmethyl with a variable admixture of its additive derivative.

The results with decane deserve particular mention. Here again, as with octane, it is possible to get from the hot solutions unchanged triphenylmethyl. But in several instances we have succeeded in obtaining the true additive derivative. This additive compound with decane differs, however, from all other analogous compounds in that it consists, apparently, of the *monomolecular* triphenylmethyl in combination with the solvent. Nor are we without an adequate explanation for this unusual behavior. It is now well established that the dimolecular triphenylmethyl—whatever its constitution may be—dissociates with the rise of temperature of the solvent into the monomolecular free radical, so that at 80° the dissociation may reach as high as 25%.¹ Decane boils at about 155° , and at that temperature triphenylmethyl must be monomolecular to a very large extent. Should separation of the solute occur at a temperature when the monomolecular phase predominates, then the additive compound will have the composition $R_3C.C_{10}H_{22}$, provided, of course, that the high temperature at which this crystallization occurs is still favorable for the formation of the additive derivative. This, evidently, is what happened in our experiments. It will be noticed in some of our results, that the percentage of the additive solvent falls short of that calculated for the monomolecular, but is nonetheless too high for the dimolecular triphenylmethyl. It must remain undecided whether in these cases we are dealing with a mixture of free triphenylmethyl and its additive compound, $R_3C.C_{10}H_{22}$, or with a mixture of the two additive compounds $R_3C.C_{10}H_{22}$ and $[R_3C]_2.C_{10}H_{22}$.

Of course, the high percentage of additive solvent might be explained by assuming the formation of the additive compound $[R_3C]_2(C_{10}H_{22})_2$ but the explanation here given seems to us preferable to this alternative.

With cyclohexane and methylcyclohexane, in which triphenylmethyl is quite soluble, the products crystallized at comparatively low temperatures, and the additive compounds were found to possess the normal composition.

To sum up, it has been shown in this paper that triphenylmethyl actually possesses the capacity to form additive compounds with completely saturated aliphatic and alicyclic hydrocarbons. Furthermore, it appears probable, that under certain conditions the monomolecular, instead of the dimolecular, modification of triphenylmethyl enters into these additive derivatives. No explanation based upon the valence hypothesis can satisfactorily account for the existence of such additive compounds.

ANN ARBOR, MICH.

¹ THIS JOURNAL, 36, 1166 (1914).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

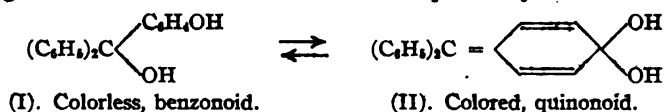
TRIPHENYLMETHYL. XXV. PREPARATION OF *p*-HYDROXY-TRIPHENYLCARBINOL AND ATTEMPTS TO ISOLATE THE CORRESPONDING TRIARYLMETHYL.

BY M. GOMBERG AND R. L. JICKLING.

Received August 26, 1915.

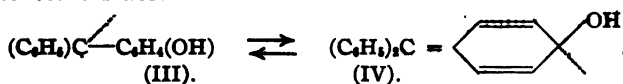
I. Introduction.

It has been shown lately¹ that a hydroxyl group in the triarylcarbinols, particularly in the *p*-position to the central carbon atom, increases greatly the tendency of the compound towards tautomerization. Triphenylcarbinol is known only in one, the colorless, state; its *p*-hydroxy derivative, however, has been obtained² in two distinct forms, the colorless and the colored, separable from each other and either readily changeable into the other merely by choice of suitable solvent. The distinctive behavior of these two carbinols is best explained, as has been shown, by assigning to them the two constitutions, respectively



The significance of this fact is evident. The existence of two desmotropic carbinols in equilibrium with each other implies, of itself, the theoretically probable existence of two desmotropic series of carbinol salts, each series derivable from its corresponding carbinol. Thus the hypothesis of the quinonoid structure of the colored carbinol salts, deduced previously wholly from the behavior of these salts themselves, receives strong additional support in the existence of the two desmotropic carbinols.

In view of the marked tautomerizing influence of the hydroxyl groups in the carbinols and in their salts, the questions naturally arise: What influence would a *p*-hydroxyl group in triphenylmethyl exert as regards the tendency of the free radical toward tautomerization? Would *p*-hydroxytriphenylmethyl, like the simple triphenylmethyl, exist as two forms in solution only, and as a solid, colorless? Would this *p*-hydroxylated free radical exist even as a solid in the two desmotropic forms (III) and (IV), as in the case with the corresponding carbinol? Or might the quinoid form of the *p*-hydroxytriphenylmethyl be the only one obtainable in the solid state?



For the preparation of the free radical *p*-hydroxytriphenylcarbinol

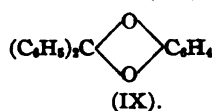
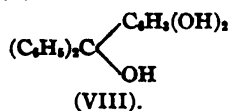
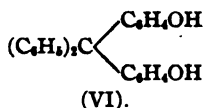
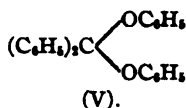
¹ Gomberg and West, *THIS JOURNAL*, **34**, 1533 (1912).

² Gomberg, *Ibid.*, **35**, 1035 (1913).

must serve as the starting point. The methods previously used to prepare this carbinol are both tedious and extended. A far simpler synthesis has been devised during the course of this work, and since this method has proved to be efficacious in the preparation of many homologous and analogous hydroxy derivatives, a detailed study of the same has been undertaken.

II. The Reaction between Benzophenone Chloride and Phenol.

In an unsuccessful attempt to prepare diphenoxydiphenylmethane (V) by the reaction of sodium phenoxide on benzophenone chloride, Mackenzie¹ obtained instead di-*p*-hydroxytetraphenylmethane (VI). He also noticed that the same product resulted from the direct action of phenol itself on benzophenone chloride. Through use of an analogous reaction, Smedley² prepared di-*p*-hydroxydiphenyldiphenylenemethane (VII) from fluorenone chloride and phenol. Zincke³ made use of the reaction mentioned by Mackenzie, and obtained the same di-*p*-hydroxytetraphenylmethane, using a large excess of phenol and heating on the water bath for three days. On the other hand, Caro and Graebe,⁴ long ago, condensed monohydroxybenzophenone chloride, and also dihydroxybenzophenone chloride, with phenol, employing sulfuric acid as the condensing agent, and obtained some benzaurine and aurine, respectively. More recently, Sachs and Thonet⁵ have condensed benzophenone chloride with catechol, also by means of absolute sulfuric acid, and have obtained 3,4-dihydroxytriphenylcarbinol (VIII), but in the absence of sulfuric acid the ether of constitution (IX) was the principal product formed.



Thus there were some indications in the literature that ketochlorides may be made to condense with phenols so as to yield a triarylcarbinol. As a rule, Friedel and Craft's reaction is seldom employed for condensations involving phenols. We found, however, that *p*-hydroxytriphenylcarbinol could, indeed, be obtained by this reaction from benzophenone chloride and benzene, fairly pure and in tolerably good yield, when carbon disulfide was employed as a solvent. At the same time we observed

¹ *J. Chem. Soc.*, 79, 1209 (1901).

² *Ibid.*, 87, 1252 (1905).

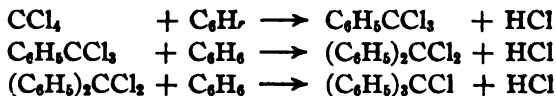
³ *Ann.*, 363, 279 (1908).

⁴ *Ber.*, 11, 1350 (1878).

⁵ *Ibid.*, 37, 3329 (1904).

that phenol acts directly without the help of the catalyst, upon benzophenone chloride in absence of solvent at room temperature. A careful study of the reaction between benzophenone chloride and phenol has been undertaken, and it has been found that the condensation proceeds in several successive steps. By observing the proper conditions during the course of the reaction, it is possible to get as the result almost exclusively any one of the three products: diphenoxy-diphenylmethane, *p*-hydroxy-triphenylcarbinol, or di-*p*-hydroxytetraphenylmethane. The most suitable conditions for the preparation of each of these products will be given first, and an interpretation of the mechanism of this whole condensation reaction follows.

The Preparation of Benzophenone Chloride.—In studying the Friedel and Crafts synthesis, Boeseken¹ found that the reaction between carbon tetrachloride and benzene under the influence of the catalyst, aluminium chloride, proceeds in at least three steps:



He was unable to isolate benzotrichloride, but by using an excess of carbon tetrachloride he obtained benzophenone chloride in good yield. We desire to emphasize the value of this reaction as an excellent means for the preparation of benzophenone chloride in large quantities.

We have obtained, by employing this reaction, benzophenone chloride in 90% yields by observing the following procedure: In a wide-mouth, two-liter bottle, 135 g. (1 mol) finely-divided aluminium chloride are suspended in 300 cc. carbon tetrachloride. To this are added through the course of an hour or more, 156 g. (2 mols) of benzene, mixed with about an equal volume of carbon tetrachloride. By cooling and shaking, the reaction mixture should be kept below 30°. The following morning the aluminium chloride is decomposed in the same bottle, preferably glass-stoppered, by adding a considerable quantity of ice at once and shaking vigorously. The temperature of the mixture is lowered to such an extent by the ice and the hydrochloric acid that hydrolysis of the benzophenone chloride is reduced to a minimum. The carbon tetrachloride solution, after drying over calcium chloride, is concentrated and the residue distilled in vacuum. The resulting product contains, as a rule, 90–95% benzophenone chloride, the balance being benzophenone. Redistillation in vacuum after addition of the calculated amount of phosphorus pentachloride gives pure benzophenone chloride.

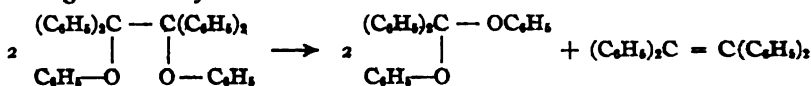
Preparation of Diphenoxydiphenylmethane.—Mackenzie in his attempts to prepare diphenoxydiphenylmethane did not study the reaction between benzophenone chloride and phenol in any other solvent than an

¹ Boeseken, *Rev. d. trav. chem.*, 24, 1 (1905).

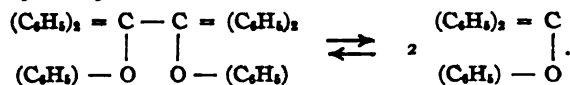
excess of phenol, and for this simple reason failed. By carrying out the above reaction in benzene we have prepared the diphenoxy compound. The formation of this compound constitutes the first stage in the action of phenol upon benzophenone chloride, and in the presence of a solvent the reaction stops here and does not proceed any further.

Molten phenol was added slowly to an equal weight of benzophenone chloride mixed with about ten times its volume of benzene, the reaction mixture being kept at about 50°. A stream of dry air was drawn, under slight vacuum, through the mass to remove the hydrogen chloride as formed, and thus prevent the decomposition of the diphenoxy derivative. Concentration of the benzene solution and addition of petroleum ether gave the diphenoxydiphenylmethane in clusters of white needles melting at 132° after recrystallization from alcohol. The yield was about 85% of the calculated amount.

Wieland¹ described as diphenoxydiphenylmethane a compound which he had obtained by heating the diphenyl ether of benzpinacolone to 280°, resulting assumably as follows:



A sample prepared according to Wieland's method was found to be identical with the product from the reaction of benzophenone chloride and phenol in benzene solution. The melting point of a mixture of the two corresponds to that of either product, 132°. Thus our results corroborate Wieland's conclusion as regards the constitution of the diphenoxy derivative. Consequently, they also lend support to his conception of the constitution of the above mentioned diphenyl ether of benzpinacolone and that of its dissociation product, the corresponding free radical, diphenylphenoxymethyl



Diphenoxydiphenylmethane is far more stable than dimethoxydiphenylmethane and its homologs, which, as described by Mackenzie, suffer decomposition even upon exposure to the air. Neither boiling water nor normal alkali has any effect upon the diphenoxy derivative. On the other hand, like its analogs, diphenoxydiphenylmethane is hydrolyzed by dilute acids, even by acetic acid, into benzophenone and the corresponding alcohol, *i. e.*, in this case, phenol.

Preparation of Hydroxytriphenylcarbinol.—Bistrzycki and Herbst² first prepared *p*-hydroxytriphenylcarbinol through elimination of carbon

¹ Ber., 44, 2554.

² Ibid., 34, 3073 (1901); 35, 3133 (1902).

monoxide from *p*-hydroxytriphenylacetic acid by means of concentrated sulfuric acid. This step is accomplished with satisfactory yield, although the preparation of the acid by condensation of mandelic acid with phenol involves a rather laborious process. Baeyer and Villiger¹ obtained the identical product by demethylating *p*-methoxytriphenylcarbinol by boiling the latter in a mixture of acetic and sulfuric acids for twelve hours, the methoxy carbinol having been prepared by Grignard's synthesis from anisic ester and phenyl bromide. Gomberg² demethylated the methoxy carbinol by means of aluminium chloride in benzene solution, a method which gives at the same time more or less diphenylquinomethane and other by-products. A highly satisfactory method of preparing this carbinol is offered by the reaction of benzophenone chloride and phenol under the following conditions: Molten phenol (3-4 mols) is chilled in a flask in such a way as to be evenly distributed on the interior surface. Benzophenone chloride (1 mol) is then added, the mouth of the flask being protected by a calcium chloride tube. The reaction begins at once with evolution of hydrogen chloride, and an occasional rotation of the flask brings fresh portions of the phenol into reaction. After ten hours or more at a temperature between 20 and 25°, the mass is subjected to steam distillation in the same flask to remove the excess of phenol. The residue is digested with 5% alkali and the alkaline solution extracted with ether in order to remove any benzophenone which may be present.³ After filtration the dissolved ether is removed from the alkaline solution by a stream of air. Addition of ammonium chloride or treatment with carbon dioxide liberates the carbinol and the dihydroxy-tetraphenyl compound in the form of a paste, which changes on standing to a granular mass. As a means of separation of the carbinol from the tetraphenyl derivative, a small amount of which is also likely to be formed together with the triphenyl-carbinol, either alcohol or 95% acetic acid may be used, as the tetraphenylmethane compound is soluble in either solvent to an extent of not more than 0.1 g. in 100 cc. Using about 6 cc. alcohol to each gram of the mixed products dissolves the carbinol and leaves a fine suspension of the tetra compound. The filtration, often quite troublesome, may be facilitated by the addition to the alcoholic suspension of a few cc. of a concentrated aqueous

¹ *Ber.*, 36, 2791 (1903).

² *THIS JOURNAL*, 35, 209 (1913).

³ This extraction is necessary at this point not only to remove the benzophenone in suspension but also the benzophenone held in solution by the sodium salt of the carbinol. The solubility of benzophenone under these conditions has been verified by a blank experiment in which it was found that benzophenone, insoluble itself in alkali, was jointly soluble with the carbinol in *n*-NaOH. In the extraction a large amount of ether is to be avoided since the carbinol through hydrolysis of its salt is also removed to some extent by this solvent.

solution of sugar. Addition of water and a few drops of ammonium hydroxide to the alcoholic filtrate precipitates the carbinol in a beautiful crystalline form. Though hardly essential, the carbinol may be recrystallized from benzene in order to remove traces of the tetraphenyl derivative.

Following the above method we have obtained with samples of 12-18 g. of benzophenone chloride yields of 90 to 98% of the calculated amount of the carbinol, with but a few hundred milligrams of the by-product, di-*p*-hydroxytetraphenylmethane. The difficulty of controlling the temperature of the viscous reaction mixture may cause at times the formation of a gram or more of the tetra compound and a corresponding decrease in the yield of carbinol. If only two mols of phenol are taken for condensation with one mol of the ketochloride the reaction mixture may be allowed to stand longer, 3-4 days, without fear of having much of the tetraphenyl compound formed. A few typical examples, tabulated below, will serve as illustration:

Chloride.	Phenol.	Temperature.	Time.	Carbinol.	"Tetra."
12	10	40-50°	1 hr.	8.7 g.	0.2 g.
12	20	0-20	1	8.0	0.3
12	17	25-35	1	10.8	1.8
12	20	20-25	15 hrs.	13.4	1.2

Preparation of Di-*p*-hydroxytetraphenylmethane.—As has been mentioned, this product is obtained when benzophenone chloride and phenol are heated together. The use of sodium phenolate dissolved in excess of phenol, is, we believe, without any advantage in this reaction. Nor is it necessary to heat the reaction for the length of time given by Zincke, three days. According to our experience, the reaction is practically completed at the end of a few hours, with a yield of 90-95% of the calculated amount.

Since di-*p*-hydroxytetraphenylmethane is the final product in the series of the three successive reactions between benzophenone chloride and phenol, it should then be possible to prepare it under suitable circumstances from any of the two intermediate products. This is in reality the case, as will be shown in discussing the mechanism of the reaction.

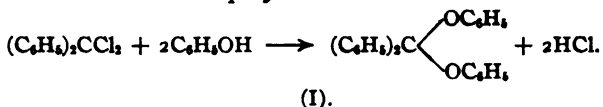
Di-*p*-hydroxytetraphenylmethane crystallizes from acetic acid in glistening, white flakes or needles, melting at 286° without decomposition. It forms a diacetyl derivative by boiling in three times its weight of anhydride together with a small amount of sodium acetate, as described by Zincke.

Mechanism of the Reaction.

The reaction between benzophenone chloride and phenol proceeds, as mentioned, in several steps.

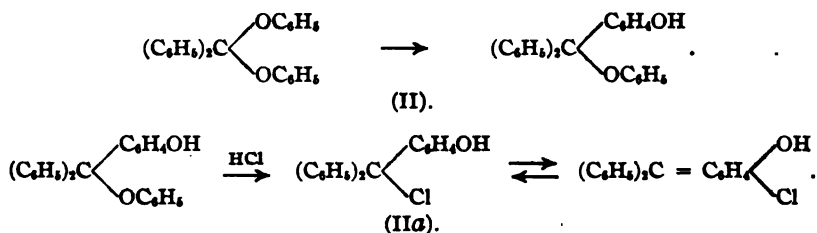
(1) The first stage of the reaction consists most probably in the forma-

tion of the diphenylether of benzophenone, whatever the experimental conditions of the method employed.



If the hydrochloric acid is being removed as formed, the reaction stops here, and the ether is the final product. Thus, the ether is formed when the chloride and the phenol are allowed to act upon each other in the presence of a solvent like benzene or carbon disulfide, in either of which the hydrochloric acid is but little soluble. But when no such solvent be present, then the viscous reaction mixture, containing during the course of the reaction always an excess of phenol, retains a certain amount of the hydrochloric acid, and the concentration of this acid becomes relatively great. The diphenyl ether, as soon as formed, is then subject to the action of the acid, and then there ensues the second stage of the condensation.

(2) In the second stage of this reaction the diphenoxy compound suffers an *intramolecular rearrangement* with respect to but one of the phenoxy groups (II). The resulting monophenyl ether, like all similar compounds, must be, to some extent, decomposed by hydrogen chloride with the formation of the chloride of *p*-hydroxytriphenylcarbinol, which, as has been shown, exists largely in the quinoid state (IIa). This latter reaction is, however, quite subordinate, but enough of the quinonoid chloride is formed to account for the intense fuchsine-like color of the reaction mixture at this stage.

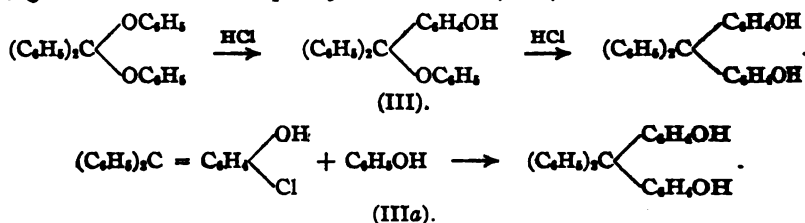


If the condensation be now stopped, after the reaction mixture has stood 1-3 days, and the whole treated with water, then the monophenoxy-ether, as well as the carbinol chloride, will yield by hydrolysis chiefly *p*-hydroxytriphenylcarbinol as the final product.

The following experiments illustrate the ease with which the diphenoxy compound undergoes an intramolecular rearrangement with respect to but one phenoxy group when subjected to the action of acid at room temperature, and with regard to both phenoxy groups at higher temperature. In a quantitative experiment 1.45 g. of substance gave, when ex-

posed to an atmosphere of dry hydrogen chloride at room temperature, 0.67 g. *p*-hydroxytriphenylcarbinol but no di-*p*-hydroxytetraphenylmethane. A 3 g. sample, when treated similarly but at 50°, gave 1.3 g. of the carbinol and 0.5 g. of the tetra compound, together with some unchanged diphenoxy derivative.

(3) But if, instead of hydrolyzing the reaction mixture after 2-3 days' standing, the reaction be allowed to proceed still further, then the process enters upon its third stage. The monophenoxy compound suffers in its turn, under the influence of the hydrochloric acid, an intramolecular rearrangement with respect to the second phenoxy group, and di-*p*-hydroxytetraphenylmethane is formed (III). At the same time, the variable, but never large, amount of chloride produced in (IIa) condenses with phenol, in the presence of the anhydrous hydrochloric acid, and it too, gives the same tetraphenyl derivative (IIIa).



That the pure diphenoxymethane can actually be changed by hydrochloric acid at elevated temperatures (50°) to the tetraphenyl compound has already been shown. The following experiment illustrates the condensation of the carbinol chloride with phenol:

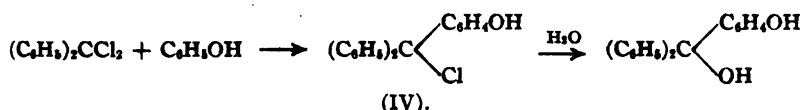
Hydrochloric acid gas was passed into a mixture of 4 g. *p*-hydroxytriphenylcarbinol and 10 g. phenol at 50° and, after a short time, 3.5 g. of the tetra compound were isolated. In acetic acid solution, 3 g. carbinol and 3 g. phenol gave, after passing in hydrogen chloride, 2.8 g. of the tetraphenyl derivative.

Thus, it will be seen that di-*p*-hydroxytetraphenylmethane is the result of three successive reactions, one etherification and two intramolecular rearrangements. The velocity of the second intramolecular rearrangement must be very much slower than that of the first, so that at room temperature, even after several days' standing, there is but little of the tetraphenyl derivative formed as compared with the amount of the triphenylcarbinol.

Every intermediate product mentioned in the explanation here offered as to the mechanism of the condensation reaction has been isolated, except one, the monophenyl ether of *p*-hydroxytriphenylcarbinol. We have not succeeded in synthesizing it, in any way, directly from the carbinol. And it is not surprising, if we may judge from the extreme sensitivity towards hydrolyzing agents of its nearest analog and proto-

type, monophenoxytriphenylmethane.¹ We have, however, obtained very satisfactory evidence in regard to the formation of our monophenoxy compound in an indirect manner.

An examination of Equations I and II will show that on this basis for every molecule of benzophenone chloride *two molecules of phenol* must take part in the reaction. On the other hand, should the formation of the carbinol proceed according to the simple scheme (IV) then only one mole-



cule of phenol would be required for the formation of the carbinol. Hence, the amount of phenol, whether one or two mols, requisite for a quantitative, or approximately quantitative, yield of the carbinol from one mol of the ketochloride serves to decide whether the monophenoxy compound is really formed as the intermediate product in the condensation or not.

The results given in Table I were obtained by carrying out the experiments with all due precautions as to purity of materials employed and constancy of temperature (20–22°), etc. On the assumption that in the experiments of Series I and II all the benzophenone chloride entered into condensation, the calculated yield of the carbinol is 8.96 g. When at the same time some tetraphenyl derivative is produced a correspondingly smaller yield of the carbinol is, of course, to be expected.

TABLE I.

Time of reaction.	Series I. RCCh + C ₆ H ₅ O 7.7 g. + 3 g. gave		Series II. RCCh + 2C ₆ H ₅ O 7.7 g. + 6 g. gave		Series III. 2RCCh + C ₆ H ₅ O 15.4 g. + 3 g. gave	
	Carbinol.	Tetra.	Carbinol.	Tetra.	Carbinol.	Tetra.
After 2 days.....	3.88 g.	None	6.05 g.	None	3.15 g.	None
After 10 days.....	4.62	None	7.42	0.43	3.95	None
After 20 days.....	5.61	Trace	7.39	0.87	4.25	None
After 30 days.....	6.00	0.11	7.73	0.93	4.76	None

A comparison of the results obtained in the two sets of experiments, Series I and II, shows plainly that two molecules of phenol give not far from the theoretical amount of the carbinol at the end of ten days, 87%, while with one molecule of phenol only a little more than half of that amount of the carbinol is obtained, *i. e.*, 51%. With the increase of the time the difference between the results in I and II becomes less, but the difference in the yields still remains sufficiently pronounced to make it apparent that two molecules of phenols are requisite in order that the one molecule of the ketochloride should be completely used up in the condensation.

¹ Baeyer, *Ber.*, 42, 2625 (1909).

In other words, if the monophenyl ether is actually an essential intermediate product in the formation of the *p*-hydroxytriphenyl carbinol, and if the condensation thus involves one molecule of benzophenone chloride with two molecules of phenol simultaneously, then we are dealing, fundamentally, with a trimolecular reaction. But if, on the other hand, the condensation is not as complex as here intimated, and if it proceeds according to Equation IV, then, clearly, we are dealing strictly with a dimolecular reaction. However, while, on the one hand, the velocity of reaction may perchance vary in a dimolecular irreversible reaction according to which of the two components is increased in amount, and is thus made to function as solvent, on the other hand, the yield of the product should be the same in both cases when, at the end of a reasonable period of time, the final equilibrium has been practically reached.

An inspection of the results of the experiments in Series II and III in Table I shows the following: With one mol ketochloride and two mols phenols the yields are 67, 86, 92 and 97% at the end of 2, 10, 20 and 30 days, respectively. With two mols ketochloride and one mol phenol the yields for the same intervals are: 35, 44, 47 and 53. Indeed, the comparison of the experiments in Series II and III shows convincingly that the reaction is not dimolecular, and that *two* molecules of phenol are essential for a quantitative yield of the triphenylcarbinol.

The fact, however, that even with one molecule of phenol, Series I, a yield of the carbinol amounting to 70%, instead of the expected 50, is reached finally at the end of a month, is quite readily explained by the subordinate reaction IIa. As therein indicated, phenol is being regenerated, and this, in its turn, will combine with some more unused benzophenone chloride. That the reaction IIa is slow, and that it soon reaches the conditions of equilibrium, can hardly be doubted, for otherwise how could diphenoxydiphenylmethane be formed so readily and so completely as it does in reality form in the first stage of the condensation?

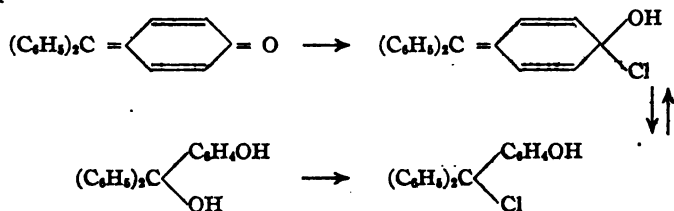
The condensation here described has been studied so much in detail because of the promise that this reaction might find application in the synthesis of other hydroxylated triarylcarbinols. Results that have been obtained in this laboratory so far indicate that in reality it may find such application, but that, at the same time, individual ketones and phenols may show a deviation from the general course of this reaction.

III. Concerning the Free Radical, *p*-Hydroxytriphenylmethyl.

The general method for the preparation of free radicals in the triaryl methyl series consists in subjecting the triarylmethyl halide to the action of metals.

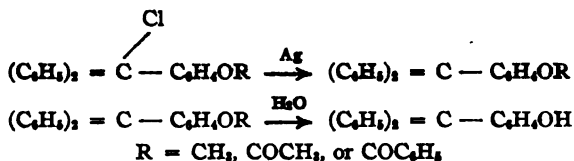
Unfortunately, *p*-hydroxytriphenylcarbinol chloride cannot be used according to this general reaction. This had also been found to be the case with

the chlorides of *p*-hydroxybenzo- γ' -pyranols¹ and of *p*-hydroxyxanthenols.² The cause for this exceptional behavior we believe to be the same in all cases, namely, the chlorine and the hydroxyl group are linked to one and the same carbon atom in these carbinol chlorides. The formation of the above *p*-hydroxy chloride takes place by exposing in the solid form either fuchson or *p*-hydroxytriphenylcarbinol to gaseous hydrochloric acid. The resulting products are identical, hence we must assume the usual equilibrium between the two tautomeric isomers.



On treatment with molecular silver a molecule of *hydrogen chloride* is split off instead of the usual single chlorine atom, giving consequently fuchson and not the free radical, *p*-hydroxytriphenylmethyl.

From these results it became evident that the only promising procedure for the preparation of the free radical would be through protection or alteration of the *p*-hydroxyl group, according to the following scheme:



in which

Realizing, however, the difficulties usually encountered in the removal of any of these protecting groups, we turned first to the carboalkoxy groups, used so extensively and successfully by Emil Fischer as a temporary protection of hydroxyl groups, in his recent studies on tannins. A carboalkoxy group is readily removed through hydrolysis, thus restoring the hydroxy compound.

p-Carboethoxytriphenylcarbinol, C₂H₅O.CO.OC₆H₄.(C₆H₅)₂COH.—Fourteen grams *p*-hydroxytriphenylcarbinol are dissolved in 55 cc. normal sodium hydroxide solution and a considerable amount of ice added to the solution. To the suspension of the sodium salt of the carbinol are added with vigorous stirring 6 g. (1.1 mol) chlorocarbonic ester. The resulting stiff paste upon becoming granular is filtered out. After drying partially, the product is recrystallized from alcohol by addition of water. The yield is quantitative. *p*-Carboethoxytriphenylcarbinol is readily solu-

¹ Gomberg and Cone, *Ann.*, 370, 203 (1909).

² Gomberg and West, *This Journal*, 34, 1562 (1912).

ble in benzene, ether, etc., crystallizing from these solvents upon addition of petroleum ether as white needles, melting at 119° .

***p*-Carboethoxytriphenylcarbinol Chloride.**—According to the usual method of preparing triarylcarbinol chlorides, this chloride is formed by passing gaseous hydrochloric acid into a benzene solution of the carbinol in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride, which, after washing with a mixture of ether and petroleum ether, melt at 98° .

Calc. for $C_{26}H_{19}O_2Cl$: Cl, 9.67. Found: Cl, 9.62.

The Action of Metals.—As has been mentioned, the usual result of the action of molecular silver or other metals on the chlorides of the triarylcarbinols in solution is the formation of the free radical with carbon in the trivalent state. The unsaturated nature of this class of compounds is illustrated, among others, by the avidity with which they unite with oxygen to form peroxides.



So characteristic is this reaction, that the isolation of the peroxide is now generally accepted as sufficient evidence of the existence of the corresponding free radical, though even temporary. Tested in this manner the carboethoxy-chloride gives rise unquestionably to its free radical.

***p*-Carboethoxytriphenylmethyl Peroxide.**—When treated with molecular silver out of contact with air a benzene solution of *p*-carboethoxytriphenylcarbinol chloride assumes, after several hours, a dark, cherry red color. On exposure to air this color disappears in a way analogous to that in the case of triphenylmethyl. Evaporation of the filtered benzene solution and washing the residue with ether to remove any unchanged chloride gives a relatively small amount of the peroxide, which, when crystallized from benzene, melts at 171° . Much better yields of the peroxide result from boiling the chloride and silver in benzene with a stream of dry air passing through the solution. Like other triaryl peroxides, *p*-carboethoxy peroxide is but slightly soluble in benzene and nearly insoluble in ether.

Calc. for $C_{26}H_{19}O_3$: C, 76.05; H, 5.52; Mol. wt., 694. Found: C, 75.73; H, 5.56; Mol. wt., 701.

All attempts to obtain the dihydroxy-peroxide by removing the carboethoxy groups alone in this peroxide resulted in the splitting of the product either to *p*-carboethoxytriphenylcarbinol or to *p*-hydroxytriphenylcarbinol. Warming the solution of the peroxide in a mixture of acetic and sulfuric acids (4 : 1) gives the former carbinol in good yield. The peroxide is not affected by boiling with a normal solution of alkali in water, but sodium ethoxide or a solution of potassium or barium hydroxides in methyl alcohol decomposes it to the hydroxy-carbinol.

Isomerization of the Free Radical.—The formation of the above-described peroxide proves definitely that the free radical, *p*-carboethoxy-triphenylmethyl, is formed as the initial step of the reaction between the chloride and molecular silver. We next attempted to isolate the unsaturated free radical in the solid state by concentration of the colored solution of the same in an atmosphere of carbon dioxide. But the residue thus obtained proved to be colorless, was found to be entirely devoid of unsaturated properties, and would no longer yield a peroxide on exposure to air, either as the solid or in solution. Consequently we may assume that the free radical exists only temporarily, and must have been affected in some way during the subsequent stages of its isolation. In fact, even in the preparation of the peroxide through simultaneous action of silver and air upon the chloride, there is formed, as a coating on the silver, more or less of this colorless, saturated compound in addition to the peroxide. More of this substance, and relatively less of the peroxide, is obtained if the solution of the free radical is kept for some time previous to oxidation; still more, if the solution is heated. It is thus not surprising that we find upon boiling the benzene solution of the chloride with silver for several hours, that practically none of the peroxide can then be obtained. For under such treatment, the reactive free radical is transformed completely into this colorless, inert substance.

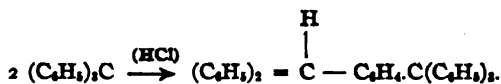
This new product is a white, amorphous powder insoluble in ether and but slightly soluble in boiling benzene or acetic acid. It melts at about 280° without decomposition. A sample from the last mentioned solvent gave an analysis corresponding closely to that calculated for the free radical. The molecular weight, determined according to the method of Menzies, proved, however, to be approximately twice that of the free radical.

Calc. for $C_{22}H_{18}O_2$: C, 79.72; H, 5.78; Mol. wt., 331. Found: C, 79.36; H, 6.04; Mol. wt., 680, 664.

The above results indicate that this unsaturated compound is either produced from the monomolecular free radical through polymerization, or more likely, is a metamer resulting from transformation of the dimolecular modification of the free radical. A change of this kind has been proved to take place in the case of the simplest free radical in this series, namely, triphenylmethyl. It was shown by Gomberg¹ that this dimolecular free radical is changed in benzene under the influence of hydrogen chloride, as a catalyst, to a stable isomer, the constitution of which has been definitely determined by Chichibabin² as *p*-benzhydryltetraphenylmethane.

¹ *Ber.*, 36, 378 (1903).

² *Ibid.*, 37, 4708 (1904); 41, 2422 (1908); Schmidlin, "Das Triphenylmethyl," p. 24.



Later Schlenk¹ found that this same transformation is brought about by the action of metallic sodium on the free radical in ether solution. The question arises: May not a similar metamerization take place spontaneously in the case of certain other radicals? In other words, may not the change of the free radical to its stable isomer proceed even without the presence of a catalyst, acid or alkali? We consider this entirely possible, and, at the present time, this is the most plausible explanation that we can offer for the relatively impermanent existence of the free radical, *p*-carboethoxytriphenylmethyl. We have modified the methods in attempting to prepare this radical by various means—by employing different solvents, by using mercury or copper instead of silver, by concentrating the solutions at very low pressure and temperature—but the result has invariably been the formation of the same stable metamer of the free radical.

Acetoxy- and benzoxytriphenylmethyl chlorides behave in this respect entirely analogously to the carboethoxy chloride. They, too, give free radicals which isomerize to stable metamers. The occurrence of such spontaneous transformations we believe to be far more frequent than has been assumed in the past. The apparent non-existence, or rather the marked instability, of the free radicals, tri-*p*-tolylmethyl, di-*p*-tolylphenylmethyl, *p*-tolylldiphenylmethyl,² tri-*p*-anisylmethyl,³ etc., may be explained as due to a similar cause, namely, to the tendency to isomerize to more stable hydrocarbons.

***p*-Benzoxytriphenylcarbinol.**—Following the Schotten-Baumann reaction, 14 g. *p*-hydroxytriphenylcarbinol are dissolved in an excess of *N* NaOH, 14 g. benzoyl chloride added and the mixture thoroughly shaken for some time. The resulting oily precipitate solidifies on standing. Its benzene solution is extracted with 10% alkali and dried over calcium chloride. Addition of petroleum ether gives the benzoxy-carbinol in the form of small crystals, melting at 132° after recrystallization from glacial acetic acid. We have nothing to add to the properties as given by Bisztycki and Herbst.⁴

***p*-Benzoxytriphenylcarbinol Chloride.**—This chloride is prepared by saturating a benzene solution of the carbinol with hydrogen chloride in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride in nearly quantitative yield, melting point 105°.

¹ *Ber.*, 47, 1665 (1914).

² Gomberg, *Ibid.*, 37, 1627 (1904).

³ Schmidlin, "Das Triphenylmethyl," p. 153.

⁴ *Ber.*, 34, 3077 (1901).

Calc. for $C_{26}H_{19}O_2Cl$: Cl, 8.90. Found: Cl, 8.74.

***p*-Benzoxytriphenylmethyl Peroxide.**—With molecular silver, a solution of the benzoxy chloride gives the usual deep color of a free radical. On evaporation of this solution, however, a mixture of two substances is obtained, the one the inert isomer of the free radical and the other the peroxide. For identification the latter was prepared by simultaneous action of silver and oxygen on the chloride. The peroxide is slightly soluble in boiling benzene, nearly insoluble in ether, and melts at 167° with decomposition. This peroxide is also readily hydrolyzed to its corresponding carbinol by warming in a mixture of acetic and sulfuric acids.

Calc. for $C_{26}H_{19}O_4$: C, 82.29; H, 5.05. Found: C, 82.40; H, 5.40.

As in the case of *p*-carboethoxytriphenylmethyl, we were unable to isolate the free radical, *p*-benzoxytriphenylmethyl. On boiling the chloride and silver in benzene, the resulting highly-colored solution of the free radical loses its color, even during concentration, with the formation of the colorless isomer. A sample of the latter, recrystallized from acetic acid, melted at $266-9^\circ$, and gave an analysis and molecular weight corresponding closely to that calculated for the dimolecular free radical.

Calc. for $C_{26}H_{19}O_4$: C, 85.92; H, 5.27; Mol. wt., 726. Found: C, 85.70; H, 5.55; Mol. wt., 710.

***p*-Acetoxytriphenylcarbinol.**—The following procedure has been adopted for the preparation of this carbinol: 20 g. of *p*-hydroxytriphenylcarbinol and 3 g. of anhydrous sodium acetate are boiled for two hours in 50 g. acetic anhydride. The product is precipitated by pouring the above solution into 100 cc. water and, if necessary, may be recrystallized from acetic acid. It possesses the properties described by Bistrzycki for this carbinol. The large excess of acetic anhydride, as employed by him, we believe to be unnecessary in the preparation of this compound.

***p*-Acetoxytriphenylcarbinol Chloride.**—Gomberg¹ has prepared this chloride by the usual method, using calcium chloride as a dehydrating agent. We find it preferable to avoid the use of hydrogen chloride. The carbinol is suspended in an excess of acetyl chloride (2 : 3 mol) and the mixture heated until all goes into solution. The excess of solvent is removed by careful heating. Upon the gradual addition of petroleum ether and allowing to stand, the acetoxy chloride separates out slowly as white needles, melting at 88° . It is very soluble in benzene or ether but only slightly so in petroleum ether.

Calc. for $C_{21}H_{17}O_2Cl$: Cl, 10.53. Found: Cl, 10.52.

***p*-Acetoxytriphenylmethyl Peroxide.**—This peroxide must be prepared by the simultaneous action of silver and oxygen on the chloride in solution. The resulting product, after recrystallization from benzene and

¹ THIS JOURNAL, 35, 200 (1913).

ether, melts at 172° . It is readily hydrolyzed to the corresponding carbinol.

Calc. for $C_{28}H_{34}O_6$: C, 79.46; H, 5.40. Found: C, 79.67; H, 5.80.

The acetoxy polymer was produced from the free radical under similar conditions as the other two polymers from their corresponding radicals. The white, amorphous powder, after purification, gave a product melting with decomposition at $255-270^{\circ}$. In its low solubility, its nonconversion through hydrolysis into the corresponding carbinol, and its lack of unsaturated properties, this polymer resembles the other analogs as described.

***p*-Carboethoxytriphenylmethyl Ether.**—Ten grams *p*-carboethoxytriphenylcarbinol chloride, 30 g. mercuric oxide and 50 cc. benzene were sealed and shaken for a month at room temperature. The resulting solution, after warming, was filtered from the mercuric oxide and chloride and concentrated. Upon addition of petroleum ether the product separated as a yellow, crystalline mass, which, after recrystallization from benzene and absolute ether, is white and melts at 219° .

Calc. for $C_{24}H_{22}O_7$: C, 77.84; H, 5.65; Mol. wt., 678. Found: C, 77.80; H, 5.74; Mol. wt., 694.

The *p*-carboethoxy ether resembles other triaryl oxides, being very readily hydrolyzed by acids. Thus it is converted into the carbinol by boiling in acetic acid or in alcohol containing a few drops of sulfuric acid.

As a rule, the carboethoxy group is easily removed by cold dilute alkali or aqueous ammonia, acetone or pyridine being added if necessary to increase the solubility of the products.¹ Treated in this manner, *p*-carboethoxytriphenylmethyl ether does lose its carboethoxy groups, but unfortunately suffers further hydrolysis to *p*-hydroxytriphenylcarbinol. Various conditions and hydrolytic agents of alkaline nature have been employed, but as yet it has been found impossible to remove only the carboethoxy groups and thus obtain the *p*-hydroxy-ether, a substance which has been the subject of controversy in the literature.

IV. Summary.

1. A detailed study of the reaction between benzophenone chloride and phenol has been carried out. Contrary to previous reports in the literature, the reaction was found to proceed in several successive stages and the mechanism of the reaction has been studied.

2. A simple and excellent synthetic method for the preparation of *p*-hydroxytriphenylcarbinol has been devised, a method which promises to become general for obtaining analogous compounds.

3. *p*-Hydroxytriphenylcarbinol chloride on treatment with metals gives up hydrochloric acid and not chlorine, thus making it impossible to prepare the corresponding free radical according to the usual method.

¹ Fischer, *Ber.*, 46, 3257 (1913).

p-Carboethoxy-, *p*-benzoxy-, *p*-acetoxycarbinol chlorides do give the respective free radicals, but these were found to be too unstable to be isolated as such, and consequently could not be used for the preparation of the hydroxytriphenylmethyl.

4. From the experimental facts obtained, an explanation is derived to account for the impermanent character of these free radicals, which may also serve to explain similar results previously reported by others, namely, a tendency of the radicals towards spontaneous polymerization or isomerization, or both.

ANN ARBOR, MICHIGAN.

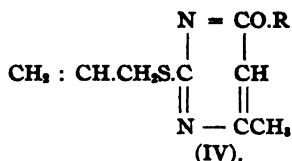
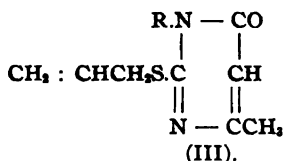
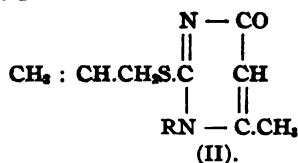
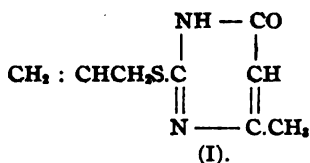
[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXXVII. THE ALKYLATION OF 2-MERCAPTOPYRIMIDINES.

BY TREAT B. JOHNSON AND ROBERT C. MORAN.

Received August 20, 1915.

Johnson and Haggard¹ made the observation that, when 2-allylmercapto-4-methyl-6-oxypyrimidine (I) undergoes alkylation in alcoholic solution and in the presence of sodium ethylate, there is no tendency, apparently, for the alkyl group of the halide to substitute in position 3 of the pyrimidine ring to form a compound corresponding to Formula II. Either an imido ester combination (IV) is formed or a mixture of this with a 1-alkyl derivative as represented by Formula III. When allyl iodide was used the corresponding imido ester (IV) ($R = CH_2:CHCH_2$) was the only product formed. In other words, the sodium salt of this pyrimidine (I) exhibited an exceptional behavior towards alkyl halides, and the presence of the negative, unsaturated, allyl mercapto group in position 2 was favorable for the formation of oxygen derivatives.



In the light of these interesting results it was of especial interest to investigate the behavior on alkylation of a 2-mercaptopyrimidine containing a more negative radical than the vinyl group $CH_2:CH-$ in the com-

¹ THIS JOURNAL, 37, 177 (1915).

pound (I). Such a radical is the benzoyl group, which is present in the pyrimidine-2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine. This compound (VIII) has already been described in a previous paper from this laboratory,¹ and is easily prepared by the action of bromoacetophenone on the sodium salt of 2-thio-4-methyl-6-oxypyrimidine.² The results obtained with the allylmercaptopyrimidine (I) suggested that, the more negative the group which we incorporate in place of a hydrogen in a 2-methylmercapto radical, the less tendency there will be for an alkyl halide to add to the 1-nitrogen atom of the ring and form a 1-nitrogen substituted pyrimidine. Oxygen compounds should then be the chief products of the reaction and if the specific group were sufficiently negative in character they would be the only products formed. The results which we have obtained by alkylation of this benzoylmercaptopyrimidine (VIII), and now described in this paper, are in accord with such an assumption.

Johnson and Moran³ observed that the sodium salt of this pyrimidine (VIII) interacts with bromoacetophenone giving exclusively the pyrimidine (VI). It therefore reacted with this halide in a manner perfectly analogous to that of the corresponding 2-allylmercaptopyrimidine (I) when treated with allyl bromide. The allylpyrimidine (I) and methyl iodide interacted to form the 1-methylpyrimidine (III) ($R = CH_3$).⁴ Our benzoylpyrimidine (VIII) reacted in a similar manner with this halide forming 2-benzoylmethylmercapto-1,4-dimethyl-6-oxypyrimidine (VII). We obtained no evidence of the formation of the imido ester combination (XI).

Besides that of methyl iodide, we have investigated the action on the pyrimidine (VIII) of ethyl bromide and benzylchloride. The former halide interacted smoothly to form exclusively the ethoxypyrimidine represented by Formula X. This same pyrimidine was also formed when the reaction was applied in methylalcohol solution. There was no evidence of the exchange of alkyl groups with formation of the imidoester (XI). The structure of our alkylated product was established by the fact that it underwent hydrolysis with formation of 4-methyluracil (XII) and 2,5-diphenyl-1,4-dithiene.⁵

When we came to investigate the action of benzylchloride on the sodium salt of the pyrimidine (VIII), in ethyl alcohol solution, we were surprised to obtain very abnormal results. In all our previous work this halide has been observed to interact smoothly in such reactions. In this case, however, we obtained no evidence of the formation of a benzylpyrimidine

¹ Johnson and Moran, *Am. Chem. J.*, **48**, 307 (1912).

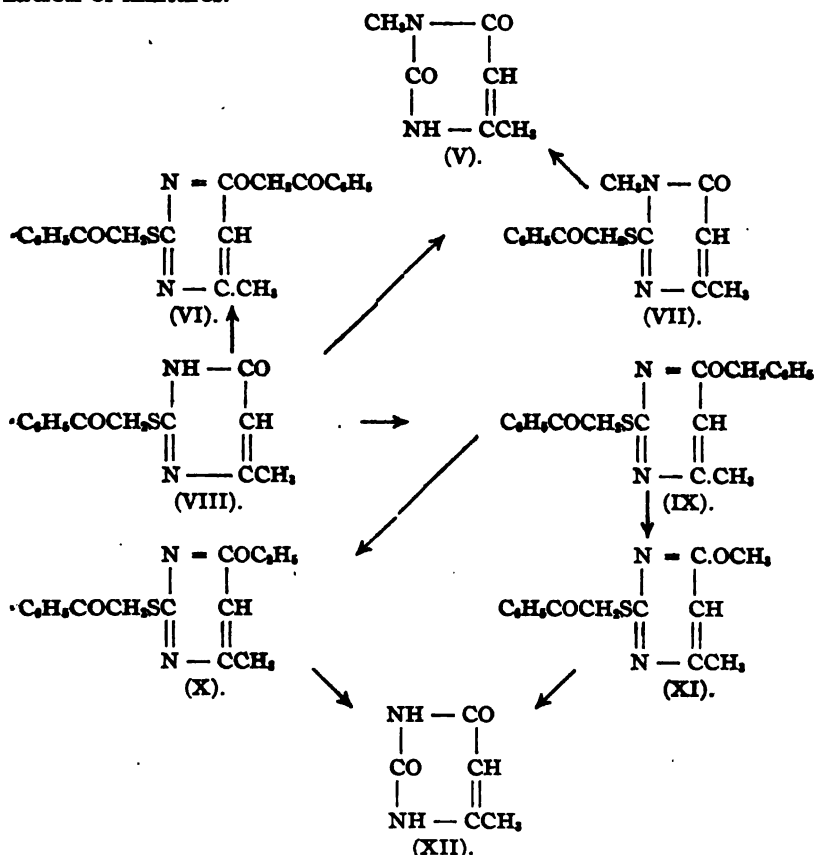
² List, *Ann.*, **236**, 3 (1886).

³ *Loc. cit.*

⁴ Johnson and Haggard, *Loc. cit.*

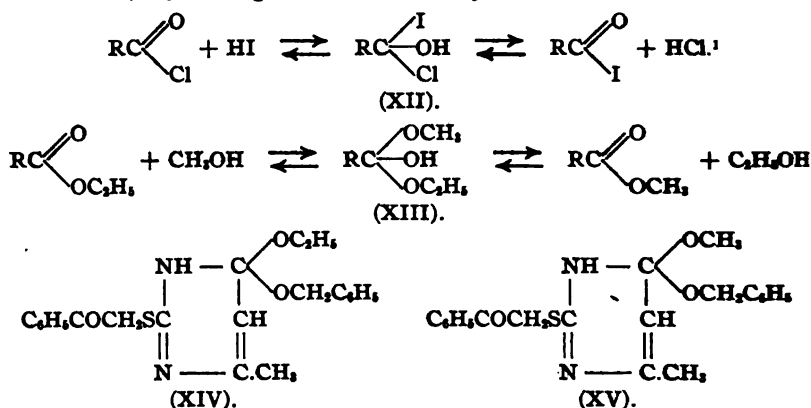
⁵ Johnson, Moran and Kohmann, *THIS JOURNAL*, **35**, 447 (1913).

corresponding to Formula IX or a 1-benzyl derivative. On the other hand, the pyrimidine interacted with the benzylchloride, in ethyl alcohol, to form the ethoxypyrimidine (X), and the yield was excellent. Furthermore, when we applied the same reaction in a solution of methyl alcohol the same abnormality was observed, and we obtained the corresponding methoxypyrimidine (XI). This is the first time that we have observed such metathetical changes in our pyrimidine investigations, and the results suggest to us why, in some of our alkylation experiments, we have experienced great difficulty in isolating pure compounds. Undoubtedly changes such as the above have taken place leading to the formation of mixtures.



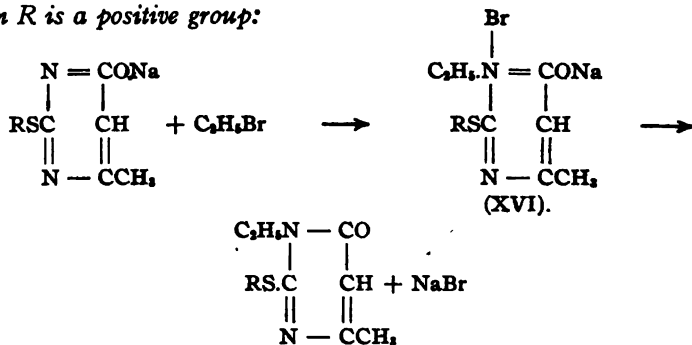
These interesting changes are analogous to those in which an alkyl group of an ester is displaced by another alcohol (XIII), and an acylchloride is converted into its corresponding iodide by the action of hydrogen iodide (XII). Intermediate addition products can be assumed to be formed in each case. In our experiment with benzylchloride the benzyl-

compound (IX) is very probably the first product of the reaction, which then adds the alcohol, serving as solvent, to form the corresponding addition compounds represented by Formulas XIV and XV. These then break down with formation of the corresponding ethoxy- (X) and methoxy-pyrimidines (XI) with generation of benzylalcohol.

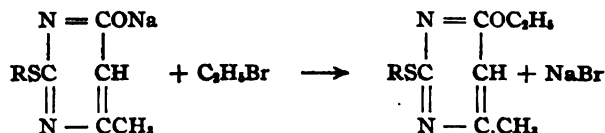


The results, which we have thus far obtained in our alkylation work, are all in accord with our previous assumption that the sodium salts of 2-mercapto-6-oxypyrimidines can interact with alkylhalides in two ways—either by addition to form nitrogen substituted pyrimidines, or by direct substitution to form oxygen derivatives. Methyl iodide generally reacts by addition to form 1- or 3-methylated pyrimidines. The two changes may be expressed by the following equations:

When *R* is a positive group:

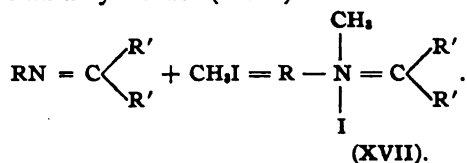


When *R* is a negative group:



¹ Standing and Anthes, *Ber.*, 46, 1417 (1913); Aschan, *Ibid.*, 45, 954; Meyer, *Ibid.*, 45, 2869 (1912); Michael, *Ibid.*, 46, 136 (1913).

The addition-product (XVI) may be viewed as a quaternary salt of a cyclic azomethine $\text{—C}=\text{N}$, corresponding to that formed by treating a Schiff base with an alkylhalide¹ (XVII).



Our researches on the alkylation of pyrimidines will be continued.

Experimental Part.

1,4-Dimethyl-2-benzoylmethylmercapto-6-oxypyrimidine (VII).—

Five grams of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine were dissolved in 50 cc. of absolute alcohol containing a molecular proportion of sodium (0.44 g.). Two and seventy-three hundredths grams of methyl iodide were then added and the solution warmed on the steam bath until neutral. The alcohol was then removed by evaporating under diminished pressure and the residue cooled, when this pyrimidine was obtained in the form of prismatic crystals. It was purified by recrystallization from ethyl alcohol and separated in stout well-developed prisms which melted at 155° to a clear oil. The yield of purified material was 2.8 g.

Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$: N, 10.22. Found (Kjeldahl): 10.51.

Hydrolysis with Hydrochloric Acid.—One gram of the above mercaptopyrimidine was suspended in 50 cc. of concentrated hydrochloric acid and the acid boiled for about one hour. A clear solution was obtained, and suspended in the liquid were globules of a yellow oil, which solidified on cooling. This was identified as 2,5-diphenyl-1,4-dithiene and melted after crystallization from alcohol at $116\text{--}118^\circ$ to a yellow oil. The acid solution was evaporated to dryness and the crystalline residue purified by crystallization from hot water. On cooling 1,4-dimethyluracil separated and melted at $259\text{--}262^\circ$ to an oil.² The yield was practically quantitative.

2-Benzoylmethylmercapto-4-methyl-6-ethoxypyrimidine (X).—This pyrimidine was formed by alkylation of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine (5 g.) with ethylbromide (2.5 g.) in the presence of sodiummethyrate (0.44 g. sodium in 50 cc. of alcohol). After cooling, and filtering off undissolved sodium bromide, the alcoholic solution was then concentrated under diminished pressure. This pyrimidine then separated as flat prisms. It was purified by crystallization from ethyl acetate and separated in flat prisms containing ethyl acetate of crystallization. They melted at 83.5° to a yellow oil. The pyrimidine

¹ Decker and Becker, *Ann.*, 395, 362 (1913).

² Behrend and Dietrich, *Ibid.*, 309, 268 (1899).

is sparingly soluble in benzene and ether, and extremely soluble in alcohol and water. Analysis (Kjeldahl):

Calc. for $(C_{11}H_{10}O_2N_2S)_2 \cdot CH_3CO_2C_2H_5$: N, 8.43. Found (Kjeldahl): 8.22, 8.31.

In a second experiment the same proportions of mercaptopyrimidine, ethylbromide and sodium were taken as above, but methyl alcohol was used as the solvent instead of ethyl alcohol. After the reaction was complete the excess of methyl alcohol and ethyl bromide were removed by evaporating under diminished pressure and the residue then triturated with ether when the pyrimidine was obtained mixed with sodium bromide. It was purified for analysis by crystallization from a large volume of petroleum ether and separated in colorless, prismatic crystals which melted at 86–88° to an amber-colored oil. The yield of crude pyrimidine was 4 g.

Calc. for $C_{11}H_{10}O_2N_2S$: N, 9.72. Found (Kjeldahl): 9.64.

Hydrolysis with Hydrochloric Acid.—One gram of this pyrimidine was dissolved in 25 cc. of concentrated hydrochloric acid and the solution boiled for several hours. 2,5-Diphenyl-1,4-dithiene was obtained as usual and melted at 116–118°. After removal of the dithiene the acid filtrate was then evaporated to dryness and the residue dissolved in hot water. On cooling a quantitative yield of 4-methyluracil was obtained. It was free from sulfur and did not melt below 280°. 1-Ethyl-4-methyluracil¹ melts at 195°.

Action of Benzylchloride on the Sodium Salt of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine.—The sodium salt of the mercaptopyrimidine was prepared as usual by dissolving 0.44 g. of sodium in 50 cc. of absolute alcohol and then dissolving 5 g. of the pyrimidine in this solution. Two and forty-four hundredths grams of pure distilled benzylchloride were then added and the solution heated on the steam bath for 3 hours, when the reaction was complete. The undissolved sodium chloride was then separated by filtration and the alcohol filtrate concentrated when a syrup was obtained, which partially solidified on cooling. This product was then triturated with ether and water and the water solution finally concentrated to a small volume and cooled. After standing for about 10–12 hours this solution finally deposited a crystalline substance, which was very soluble in water and alcohol. It was identified as 2-benzoylmethylmercapto-4-methyl-6-ethoxypyrimidine and it crystallized from ethylacetate in characteristic flat prisms melting at 83.5° to a yellow oil. A mixture of this substance and some of the pure ethoxypyrimidine from the preceding experiment melted at exactly the same temperature. We obtained no evidence of the formation of a benzyl derivative.

Calc. for $(C_{18}H_{16}O_2N_2S)_2 \cdot CH_3COOC_2H_5$: N, 8.43. Found (Kjeldahl): 8.15.

¹ Beilstein's Handbuch, I, 1351; also THIS JOURNAL, 42, 109.

Alkylation with Benzylchloride in Methyl Alcohol Solution. **2-Benzoylmethylmercapto-4-methyl-6-methoxypyrimidine (XI).**—This methoxypyrimidine was obtained by alkylation of 2-benzoylmethylmercapto-4-methyl-6 oxyypyrimidine with benzylchloride in methyl alcohol solution. The following proportions were used: 0.44 g. of sodium dissolved in 50 cc. of methylalcohol, 5.0 g. of the mercaptopyrimidine and 2.44 g. of benzylchloride. The manipulation was similar to that described in the previous experiment, and the reaction was complete after digesting on the steam bath for 12 hours. The undissolved sodium chloride was then separated by filtration and the alcohol filtrate concentrated, under diminished pressure, to a volume of 15 cc. and cooled. The methoxypyrimidine then separated and was purified by washing with ether and finally crystallizing from ethylacetate. It separated in slender needles, which melted at $143-4^{\circ}$ to a yellow oil without decomposition. The yield was 3.5 g.

Calc. for $C_{14}H_{14}O_2N_2S$: N, 10.22. Found (Kjeldahl): 10.05.

Hydrolysis with Hydrochloric Acid.—One gram of the above methoxypyrimidine was dissolved in 25 cc. of concentrated hydrochloric acid and the solution boiled for 2 hours. 2,5-Diphenyl-1,4-dithiene was obtained as usual and melted after crystallizing from alcohol at $116-117^{\circ}$ to an oil. The acid solution was concentrated to a volume of about 10 cc. and cooled when 4-methyluracil was obtained. We obtained no evidence of the formation of a benzoxypyrimidine or of 1- and 3-benzyl-4-methyl-6-oxyypyrimidines.¹

Calc. for $C_{14}H_{14}O_2N_2S$: N, 22.22. Found (Kjeldahl): 22.1.

2-Benzoylmethylmercapto-4-methyl-6-methoxypyrimidine is not converted into its corresponding ethoxy derivative (above) by warming with ethyl alcohol. It was recovered unaltered, and melting at 143° , after digesting with an excess of ethyl alcohol for 5 hours.

An attempt to alkylate 2-benzoylmethylmercapto-4-methyl-6-oxyypyrimidine in alcohol solution with ethyl chloroacetate was unsuccessful. The sodium salt of the pyrimidine was prepared by dissolving 0.44 g. of sodium and 5.0 g. of the mercaptopyrimidine, respectively, in 50 cc. of absolute alcohol and 2.36 g. of ethyl chloroacetate then added. After digesting at 100° for 5 hours the solution was neutral to turmeric and blue litmus and sodium chloride had deposited. After filtering off the salt the solution was concentrated and cooled when we obtained the original mercaptopyrimidine. It was purified by recrystallization from alcohol and separated in prismatic crystals melting at 165° to a clear oil. The experiment was repeated and the same result was obtained.

Calc. for $C_{14}H_{14}O_2N_2S$: N, 10.7. Found (Kjeldahl): 10.44.

NEW HAVEN, CONN.

¹ Wheeler and McFarland, THIS JOURNAL, 42, 101.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

STUDIES ON NITRATED PROTEINS. IV. THE IDENTIFICATION OF 3-NITROTYROSINE AMONG THE PRODUCTS OF HYDROLYSIS OF NITRATED FIBROIN.

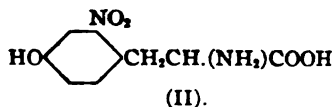
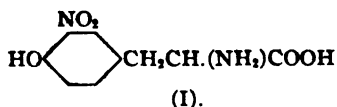
BY TREAT B. JOHNSON.

Received August 20, 1915.

In 1912, K. Inouye¹ made the interesting observation that, if silk fibroin is first nitrated under certain conditions and then subjected to hydrolysis with sulfuric acid, *nitrotyrosine* is one of the products of decomposition. The acid was separated from the other products of hydrolysis by precipitation with phosphotungstic acid, and melted, according to his statement, at 215–216°. He found by analysis 12.13 % of nitrogen, while the calculated value for an amino acid of this constitution is 12.38 %. From the acid filtrate left after precipitation of this hydrolytic product he was able to separate a second amino acid (?) having a higher melting point. From 50 g. of fibroin 0.3 g. of this substance was obtained which melted at 233–234°. This product gave on analysis 12.26% nitrogen. Inouye believed that his first product melting at 215–216° was *mononitrotyrosine* and wrote as follows regarding the second acid:

".....wich hingegen bezüglich des Schmelzpunktes von dem oben erwähnten Präparat ab und war auch bedewtend leichter löslich. Es ist hiernach wahrscheinlich, dass es sich um unreines Mononitrotyrosin handelte."

Inouye was unable to assign a definite structural formula to his nitroacid because the structure of Strecker's nitrotyrosine,² which is prepared by the action of nitric acid on tyrosine, was not known at the time of publication of his paper. The acid might be assigned one of two possible formulas (I and II), and it was not improbable that he was actually dealing with both modifications.



Since the publication of this paper of Inouye's the constitution of Strecker's acid has been established by Johnson and Kohmann³ and it was therefore of the greatest importance to obtain again Inouye's nitroacid from nitrated fibroin and compare it with the synthetical product. This has now been done, and in this paper evidence will be presented which has led to the conclusion that Inouye's acid is an ortho-nitrophenol combination corresponding to Formula I.

¹ *Z. physiol. Chem.*, 81, 82 (1912).

² *Ann.*, 73, 70 (1850).

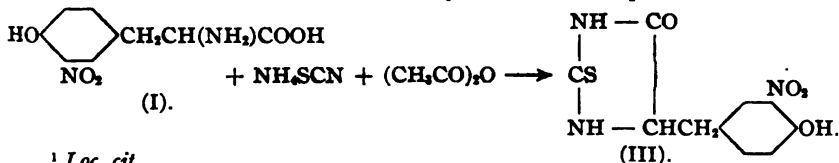
³ *THIS JOURNAL*, 37, 1863 (1915).

Johnson and Kohmann¹ have shown that tyrosine undergoes nitration, under the conditions recommended by Strecker¹ and also Städeler,² forming a mixture of the two possible isomers represented by Formulas I and II. The *ortho*-nitro compound is the chief product of the reaction. The presence of the two acids was shown by conversion into their corresponding thiohydantoin, which we succeeded in separating by fractional crystallization. The *o*-acid was observed to melt at 231° with decomposition. Its thiohydantoin derivative and that of the *m*-acid melted at 238–242° and 270°+, respectively. The *m*-acid (II) has not been synthesized.

I have now repeated the work of Inouye and find, as he has already shown, that nitrotyrosine is formed by hydrolysis of a nitrated fibroin with sulfuric acid. I first followed his directions and confirmed his observation that the acid is precipitated with phosphotungstic acid. I also examined the filtrates after this precipitation and succeeded in identifying nitrotyrosine. Both of these products were carefully examined and it is my conclusion that they are identical. In other words, Inouye only partially precipitated his nitrotyrosine with phosphotungstic acid. I examined very carefully the acids from both sources and found them to be identical with respect to crystalline habit, solubility, and their melting points. Inouye's work was repeated with slight modifications in details of manipulation, and here again only one nitroacid was obtained and it was proven by analysis to be a *mono*-nitrotyrosine. I obtained no evidence of the formation of more than one modification, nor could I detect any evidence suggesting that a *dinitrotyrosine*³ was present among the hydrolytic products.

The structure of the *nitrotyrosine* obtained by hydrolysis of Inouye's nitrated fibroin is to be represented by Formula I. It is identical with Johnson and Kohmann's *ortho*-nitroacid prepared from tyrosine and forms the same characteristic hydrochloride.

Its structure was also established in the following manner: It interacted with ammonium thiocyanate, in the presence of acetic anhydride, forming a hydantoin combination which was converted into 2-thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin (III) by hydrolysis with hydrochloric acid. This hydantoin was identical with that already described by Johnson and Kohmann.¹ Both compounds melted at 238–240° and a mixture of the two melted at exactly the same temperature.



¹ *Loc. cit.*

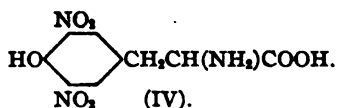
² *Ann.*, 116, 77 (1860).

³ Johnson and Kohmann, *THIS JOURNAL*, 37, 2166 (1915).

Inouye states that his nitroacid, which was precipitated by phosphotungstic acid, melted at $215-216^{\circ}$ and that the second acid which was isolated from the filtrates melted at $233-234^{\circ}$. The first melting point is too low and the latter nearly identical with that of the synthetical acid. Our acid melted at $231^{\circ}+$ with decomposition. This point of decomposition, however, is dependent upon the rate of heating and it was my experience that the melting point could be raised to $233-236^{\circ}$ if the sulfuric acid bath was heated rapidly. According to our data Inouye's second product (melting at $233-234^{\circ}$) was his purest acid, and his analytical results confirm such a conclusion.

Inouye's observation was of biochemical importance as being the first experimental evidence in support of the assumption, that the yellow color produced in the *Xanthoproteic Reaction* for proteins is dependent in part on the formation of a *mono-nitrotyrosine* combination. From the results of this investigation we are therefore able to ascribe a definite structural formula to this acid. *The aminoacid tyrosine and tyrosine linked in the protein (fibroin) are attacked in a similar manner when exposed to the action of nitric acid, and substitution of the nitro group takes place in a position ortho to the phenol group.*

Whether the second *ortho* position will be substituted by more vigorous treatment of fibroin, forming a dinitroprotein, remains to be established. Such a combination should give on hydrolysis 3,5-dinitrotyrosine (IV) which has been described in a previous paper by Johnson and Kohmann.¹



The study of nitrated proteins will be continued.

Experimental Part.

Nitration of Fibroin.—In this investigation I used the purest skein silk. It was nitrated according to the directions given by Inouye¹ and thoroughly washed with water and dried at 100° to a constant weight.

Hydrolysis of Nitrated Fibroin with Sulfuric Acid.—Fifty grams were hydrolyzed for 10 hours by digesting with sulfuric acid (100 g. concentrated acid diluted with 180 g. of water), and the sulfuric acid then exactly precipitated by addition of barium hydroxide. After filtering off the barium sulfate we obtained an orange-colored solution. This was then concentrated, by evaporation on a steam bath, to a volume of 175 cc. and the latter then examined for nitrotyrosine.

This solution was acidified with sulfuric acid, sufficient reagent being used to produce approximately a 5% solution. To this was added an excess of phosphotungstic acid, when a gummy, dirty brown precipitate was

¹ *Loc. cit.*

obtained. Part of this assumed a granulated condition while the remainder adhered to the sides of the precipitation jar. (This solution was saved.) The precipitate was washed with 5 % sulfuric acid and finally decomposed by digesting with barium hydroxide. The barium tungstate and barium sulfate were filtered off and the filtrate freed from barium by precipitation as barium carbonate. The salt was then removed by filtration and the solution concentrated to a small volume and the last traces of barium removed by adding the required amount of sulfuric acid. After filtering from barium sulfate this solution was concentrated to a small volume and allowed to stand for several days in a desiccator over concentrated sulfuric acid. I obtained about 0.75 g. of material here which crystallized in the form of burrs or rosets of small crystals. This gave Millon's reaction, when applied under special conditions,¹ and possessed all the properties of *mono*-nitrotyrosine.

The acid filtrate left behind after precipitation with phosphotungstic acid (see above) was combined with barium hydroxide to precipitate all the sulfuric acid and excess of phosphotungstic acid. The barium sulfate and barium phosphotungstate were then filtered off and, after saturation with carbon dioxide to precipitate barium as barium carbonate, the resulting solution finally concentrated to a volume of about 100 cc. This was orange-red in color and still contained barium. It was diluted with water and the barium precipitated as the sulfate by adding exactly the required amount of sulfuric acid. The solution was then filtered and allowed to evaporate spontaneously in a vacuum over concentrated sulfuric acid. After concentration to a volume of about 15 cc. crystals began to deposit. About 1.5 g. of material separated here. When first crystallized from boiling water the compound separated as corpuscular crystals which were colored brown. On repeated crystallization, however, the material grew lighter in color and finally deposited in beautiful lemon-yellow rosets or burrs of small needles (or slender prisms). These crystals began to contract at 221°, when heated in a capillary tube, and decomposed at 231° with violent effervescence, giving a black residue. This decomposition point could be raised to 233–236° by rapid heating. Millon's test was positive if carefully applied and the compound dissolved in alkaline solutions with an intense red color. It was dried for analysis at 100°. The substance was identified as *nitrotyrosine*, $(\text{NO}_2)(\text{OH})\text{-C}_6\text{H}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$.

Calc. for $\text{C}_8\text{H}_9\text{O}_5\text{N}_2$: N, 12.3. Found: N, 12.14.

Nitration of Fibroin for a Second Hydrolysis Experiment.—One hundred and sixty-six grams of the purest skein silk were used in this experiment. This was suspended in 4 liters of nitric acid of density 1.12,

¹ Johnson and Kohmann, *Loc. cit.*

and the reaction allowed to continue at ordinary temperature for 48 hours. The silk had then turned bright yellow. It was washed repeatedly with water to remove every trace of nitric acid and finally with 95% alcohol. After drying thoroughly at 80-90° the weight was 155.0 g. Therefore the loss by the treatment applied was 6.6%. If silk noils had been used for the nitration instead of the skein silk the loss in weight would have been much greater.¹

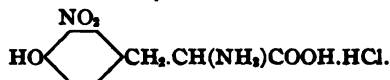
Hydrolysis of the Nitrated Fibroin.—Four hundred and sixty-two grams of concentrated sulfuric acid were diluted with 792 cc. of water, and the nitrated silk hydrolyzed by heating with this diluted acid at 125° for 11 continuous hours. On cooling the resulting solution a black, insoluble substance was obtained. This was separated, but the amount obtained was so small that it was impossible to carefully study its behavior. It was insoluble in water, but dissolved at once in aqueous ammonia and cold sodium hydroxide solution, forming black solutions which were not decolorized by digestion with bone-coal. On adding acids to the alkaline solutions the melanine-like substance was reprecipitated again in an amorphous condition. It possessed no definite melting point. It is our intention to take up again the study of this peculiar substance.

The filtered solution was treated as usual with barium hydroxide to remove all the sulfuric acid. As long as the solution was acid it was practically colorless, but just as soon as the acid was completely precipitated and barium hydroxide was added in excess the solution assumed a red color due to the formation of the barium salt of nitrotyrosine. This change was very characteristic. After filtering from barium sulfate the solution was concentrated to a volume of 145 cc. and having the consistency of a syrup. This was then allowed to stand for one week when a thick magma of crystalline material was obtained. This substance was separated from the syrupy mother liquor by filtration and then dried at 80-90°. The weight was 80 g.

This material (80 g.) was dissolved in 700 cc. of water and 40 cc. of concentrated sulfuric acid added to the solution. This acid solution was then treated with an excess of phosphotungstic acid when we obtained a heavy precipitate of the phosphotungstate of nitrotyrosine. This was separated by filtration and finally decomposed in the usual manner by digesting with a solution of barium hydroxide. The precipitate was filtered off and the excess of barium then removed by adding the calculated amount of sulfuric acid. The filtrate from the barium sulfate was nearly colorless, but turned intensely red when made alkaline. This was concentrated to a volume of about 20 cc. and the syrupy solution mixed with 2-3 times its volume of cold, concentrated hydrochloric acid. The hydrochloride of nitrotyrosine separated at once as yellow

¹ Johnson, Hill and O'Hara, *THIS JOURNAL*, 37, 2170 (1915).

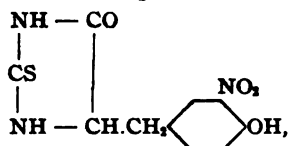
needles. The last dissolved at once in water but was reprecipitated by saturating the solution with hydrochloric acid. This salt began to change color at about 220–221° and then decomposed with violent effervescence at 233–235°. It was identified as the hydrochloride of 3-nitrotyrosine.¹



A mixture of this salt with that prepared from pure nitrotyrosine melted at exactly the same temperature. The salt was dried for analysis by heating at 100°.

Calc. for $\text{C}_9\text{H}_{11}\text{O}_5\text{N}_2\text{Cl}$: N, 10.66. Found: N, 10.66.

Conversion of 3-Nitrotyrosine from Nitrated Fibroin into Its 2-Thiohydantoin—2-Thio-4-(3-nitro-4-hydroxybenzyl)-hydantoin.¹—Five-tenths of a gram of the above hydrochloride was dissolved in dilute ammonia and the solution evaporated to dryness to decompose the hydrochloride. The dry residue was then dissolved in 10 cc. of acetic anhydride with 0.7 g. of anhydrous ammonium thiocyanate and the mixture heated at 100° for one hour. The solution was finally heated for a few minutes to its boiling point. After this treatment, an excess of dilute hydrochloric acid was added and the solution evaporated to dryness at 100°. The residue obtained was dissolved in fresh hydrochloric acid and the evaporation repeated. On triturating the residue to remove ammonium chloride I obtained the thiohydantoin insoluble in water. It was also insoluble in alcohol but crystallized from boiling glacial acetic acid in the form of diamond-shaped prisms. The substance melted at 238–239° with effervescence, turning red before decomposing. Johnson and Kohmann² observed that the thiohydantoin of 3-nitrotyrosine (synthetical material) can be heated to 242° before it will decompose. This, however, happens when the sulfuric acid bath is heated rapidly. I have observed variations of 5–6° and under normal conditions it usually will melt from 238–240°. A mixture of Johnson and Kohmann's thiohydantoin with the hydantoin prepared from the nitrotyrosine from silk melted at 238–239°. The two compounds therefore were identical and the structure of my hydantoin is to be represented by the following formula:



Calc. for $\text{C}_{10}\text{H}_9\text{O}_4\text{N}_2\text{S}$: N, 15.73. Found: N, 15.6.

The investigation of nitrated proteins will be continued.

NEW HAVEN, CONN.

¹ Johnson and Kohmann, *Loc. cit.*

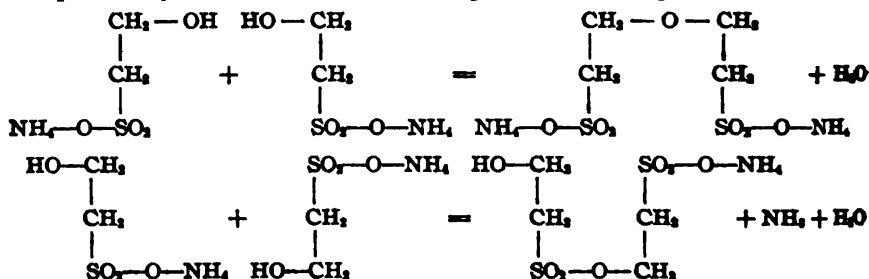
² *Loc. cit.*

NOTES.

The Change of Ammonium Isethionate by Heating.—The two authors who have investigated the change which occurs on heating ammonium isethionate have reached very different conclusions. Strecker¹ states in his paper that ammonium isethionate (ammonium hydroxyethyl sulfonate) will change to taurine with the loss of 10 to 12% in weight by heating at 220°, according to the following formula:



Carl,² on the other hand, having carried out his experiment in exactly the same manner as Strecker, found that by heating 7 hours at 210–220° ammonium isethionate is converted into ammonium diisethionate and another substance, the molecular formula of which is $\text{C}_4\text{H}_{12}\text{S}_2\text{NO}_7$, accompanied by the loss of 12% in weight. The change is as follows:



I had occasion lately to synthesize taurine, and after examining the literature concerning the synthesis of this compound, Strecker's method appeared to me to be the most convenient. I tried his method many times but did not succeed in obtaining taurine. After many trials I came to the conclusion that Strecker's reaction never occurred and the change which ammonium isethionate undergoes by heating is that reported by Carl.

In conclusion, the author wishes to express his thanks to Prof. T. B. Robertson for his kind advice in the course of this experiment.

K. MIYAKE.

THE RUDOLPH SPRECKELS PHYSIOLOGICAL LABORATORY
OF THE UNIVERSITY OF CALIFORNIA.

On the Use of Trichloroacetic Acid as a Protein Precipitant.—In a recent paper,³ Kober refers to "Greenwald's discovery of trichloroacetic

¹ *Ann. Chem.*, 91, 97 (1854).

² *Ber.*, 12, 1604 (1879).

³ Graves and Kober, *THIS JOURNAL*, 37, 2445 (1915).

acid as a reagent for the removal of blood proteins." The writer makes no claim to any such discovery. Trichloroacetic acid has long been used as a protein precipitant, and it was merely applied to a specific purpose, *vis.*, the removal of the proteins and lipins of blood in order to permit of the determination of non-protein nitrogen in the filtrate. The use of the phrase "Greenwald's reagent" is without justification.

I. GREENWALD.

HARRIMAN RESEARCH LABORATORY,
ROOSEVELT HOSPITAL, NEW YORK.

NEW BOOKS.

The First Year of Science. By JOHN C. HESSLER, PH.D., Professor of Chemistry, The James Milliken University, Late Instructor in the University of Chicago and in the Hyde Park High School, Chicago. Boston: 1914. Benjamin H. Sanborn & Co. xiii + 484 pp.

Laboratory Exercises of "The First Year of Science." By the same author and publishers (1915). ix + 118 pp.

In his very interesting preface the author states his conviction that while Physics and Chemistry, as such, should not be given in the first year of a high school course, some knowledge of these sciences is essential for all later work in any science, and that the simpler principles can be given in a course in General Science. Such a course is described in this book, and laboratory exercises are provided in the smaller volume, all of which, the author believes, can be successfully given to large classes, without special teachers, or expensive laboratory equipment. The book and the course are designed to "stimulate uncommon thinking about common things."

There are twenty chapters, twelve of which deal essentially with the fundamental principles of physics and chemistry, and their application to common affairs, but without formulas, symbols or equations. The remaining chapters deal with such topics as "Water, Heat, Air, and Light in the Home," "The Weather," "Rocks and Soils," "Plants," "Animals," three chapters on Physiology (sufficient, it is claimed, to constitute by themselves a short course in Physiology), and one on "Sanitation." The text proper and the laboratory manual are to be accompanied by a Teacher's Handbook. At the end of each chapter of the text proper there is a summary of the leading topics of the chapter, and a series of highly suggestive questions. The Appendix contains a series of useful tables, and there is a Glossary.

The Laboratory Manual includes one hundred and seven exercises, ranging through physics and chemistry (as applied to common affairs), weather records, tests upon rocks and soils, growth and study of plants, studies of the habits of the earthworm, mollusks, and insects, and some simple physiological tests. The greatest pains have been taken to sim-

plify all experimentation, and to describe utensils which, in many instances, can be made and used in the home.

This text is crowded with facts, interestingly told, which should serve to "link science with everyday things," provided only that there are not too many of them for the time allotment. The author presumably writes from experience, and a selection of topics on the part of any teacher is easy without a break in continuity of instruction. In general, the statements are clear, and sufficiently accurate in a scientific sense for the purpose of the course. In the chapter upon sanitation, however, the author has permitted himself to introduce the sensational statements and illustrations of the press, and of certain agencies which feel that they must over-state dangers in order to attract attention to them at all. This chapter seems a bit out of line with the rest of the book, and there is at least some doubt whether the entire chapter would not logically lead to a condition of nervous dread on the part of the young reader, rather than to sane precaution in time of real danger. A somewhat similar over-emphasis is to be found in the discussion of tobacco and alcohol, but possibly to good purpose.

Most of the illustrations specially prepared for this volume are admirable, but the cuts borrowed from various sources often lack distinctness and contain too much detail. It is a pity that the reader should be constantly forced to pay tribute to the loaners of these cuts, a matter in which he has no real interest.

Every teacher of science will find much of interest in these volumes, and the text proper may well be heartily recommended to the general reader who desires to acquire a knowledge of science as applied to daily life, or to the college graduate who has not found it practicable to include physical sciences in his course. It seems to be one of the best books of its class which has yet appeared.

H. P. TALBOT.

Chemical Calculations. By R. HARMAN ASHLEY, PH.D., Assistant Professor of Chemistry in the University of Maine. New York: D. Van Nostrand Company. 1915. 13 X 19 cm., pp. ix + 276. Price, \$2.00, net.

The author intends this book to follow, more closely than the other similar books, the needs of the student who will later find occupation in chemical laboratory work. Thus, while the usual types of problems of the beginners' course are dealt with, some space is also devoted to such topics as Baumé and Twaddell scales, analytical factors, formulas of minerals, titration of oleum, "mixed acid," etc.; and some articulation is effected with the tables in Van Nostrand's Chemical Annual. The poorly-trained works chemist will thus undoubtedly find the book useful.

The exposition of the broader principles is not compellingly pellucid, but the book contains many good problems and exercises. The inaccuracy

cies appear about normal in number and quality, and could in many cases have been avoided by more critical proofreading. The price of the book seems high.

ALAN W. C. MENZIES.

A Course in Quantitative Chemical Analysis, Gravimetric and Volumetric. By NICHOLAS KNIGHT, A.M., PH.D., Professor of Chemistry, Cornell College. Revised Edition. New York and Chicago: The A. S. Barnes Co. 1915. pp. vii + 153. Price, \$1.25.

This little book consists of Part I, 13 pages on general procedures; Part II, 56 pages on fifteen gravimetric exercises involving the analysis of five pure salts, two alloys, seven minerals and one rock; Part III, 17 pages on volumetric analysis including sections on indicators, general suggestions, titrations with permanganate, dichromate and silver nitrate and alkalimetry, acidimetry and iodimetry; Part IV, 12 pages on water analysis both mineral and sanitary; Part V, 12 pages of appendix, including reactions, tables, etc., and, finally, five pages of index.

It is seen from the above that the matter in this book is very concentrated. Everything is sacrificed to condensation. The sentences are short and nearly all cast in the imperative mode, as in a recipe. To save space, the author goes so far even as to eliminate two of the dimensions of space for he frequently writes "centimeter" when he means "cubic centimeter." However, barring a few slips like the above, this style of writing is very well handled and the short, imperative sentences are made to flow along with surprising smoothness.

So much is left to be imparted by personal instruction at the student's work place or to be gathered by the student in general reading, that it is difficult to criticize the sins of omission in the book. The author could with justice reply, "I give all that in my talks," or "The student gets that by referring to larger works on the subject."

It is after all a matter of opinion. The reviewer confesses to feeling that since the beginner must be told a hundred and one points in manipulation and be warned against the numerous pitfalls that beset his path, then why not arrange this matter in logical order, put it into one's best style, print it and give it to the student? It seems foolish to do otherwise than to anticipate in this way the stock blunders of beginners. It conserves the time of the instructor which can then be more profitably spent in quizzing.

There might also be some difference of opinion as to the choice of samples for analysis. Pure salts and selected minerals are used in many cases to the exclusion of more interesting commercial products that would illustrate the same principles.

The author is conservative on certain points. He writes "litre" and "centimetre" and gives the Mohr liter, which he does not define ac-

curately, as the unit of measurement in volumetric analysis. The results of water analysis are also reported in parts per 100,000.

C. W. FOULK.

Experiments in Organic Chemistry. By F. J. MOORE, PH.D. New York: John Wiley and Sons. Price, 50 cents net.

This is the second edition of Professor Moore's laboratory manual and accompanies the second edition of his "Outlines of Organic Chemistry." His text book is so well known and so widely used that the manual based upon it should need no introduction to teachers of organic chemistry. The experimental work outlined in the manual is supposed to occupy the students' time during fifteen periods of three hours each. The method of presentation of the subject is essentially that of a manual of general chemistry. The object is to acquaint a student in a short time with the characteristics of as many organic compounds as possible. The directions are concisely and clearly written, and the experiments are within the range of equipment of the most meagerly supplied laboratory. If a teacher is using Professor Moore's "Outlines of Organic Chemistry" as a text book and has the same students in the laboratory the manual would be very useful.

L. H. CONE.

Practical Physical Chemistry. Third edition, enlarged. By ALEX. FINDLAY. New York: Longmans, Green and Co. Price, \$1.20.

This book was written primarily for students of chemistry in the University of Birmingham and the experiments were selected with a view to assisting the general chemistry student to a better understanding of the laws of physical and theoretical chemistry.

The book has appealed to a much wider circle and in the third edition new experimental methods and chapters have been added as well as references to the literature for the more advanced students. It is to be hoped that this is one of the stages in the development of this book and that we will shortly have a text comparable to the Ostwald-Luther Physical Chemistry Measurements or the Kohlrausch "Leitfaden der Physik," for there is a distinct lack of such a text in the English language, and perhaps the main criticism of this edition is that it has not been very extensively enlarged.

Some references to the literature have been added to give an idea of details of more accurate measurements. These are not intended to be exhaustive but if they had been attached to the paragraphs concerned rather than at the end of chapters and without indication of the subject treated, they would be more used and useful. They should be made fairly complete.

Under vapor densities, the method first described by Bleier and Kohn, (*Monatsh*, 1899) is still called the Lumsden method. It might be well to refer to this method as the constant volume method and the Victor

Meyer method as the constant pressure method. It is possible that the Dumas method is little used, as stated, and so it is not described. This is unfortunate, if true, for it is the only method which gives reliable results with substances which dissociate and with slight modifications it is possible to determine with ease and accuracy the vapor density of acetic acid and phosphorous pentachloride at different temperatures. Such work is important for beginners as a foundation for later studies on equilibrium and dissociation in solution. The more recent methods for vapor densities described by Blackman and Menzies are included, as well as a short paragraph on the analysis of binary mixtures by the application of vapor density determinations.

In addition to the regular methods for molecular weights in solutions, a method of determining directly the lowering of the vapor pressure of the solvent as described by Menzies is given.

Under conductivity, determinations of the solubility of sparingly soluble salts and the hydrolysis of salts in solution are described, and also exercises on the solubility of gases in liquids and liquids in liquids. The measurements of decomposition and ionic discharge potentials are taken up in Chapter XI. The construction of standard cells does not correspond to modern practice and is no simpler. The value of the Weston standard at 20° is given as 1.086 instead of the International Conference value of 1.0183. Perhaps the difference is not important for the measurements contemplated, but the value should be correct as far as given.

G. A. HULETT.

The Chemistry of Colloids, and Some Technical Applications. By W. W. TAYLOR, Lecturer in Chemistry at the University of Edinburgh. vi and 328 pp.; 21 figs. New York: Longmans, Green and Co. Price, \$2.00.

The author, in the preface, expresses the hope that this book "will meet the want of a convenient text-book (in English) and at the same time serve as a reference book for workers in other sciences." The subject matter is divided into four parts: General Properties, Methods of Preparation, Adsorption, and Applications. In general the author has followed the rule of giving experimental facts and data first, then following with a brief theoretical discussion. In the section on adsorption he has reversed the usual order and introduced the subject with a theoretical discussion with the result that this section seems notably more satisfactory, to the reviewer, than the others. The working through of long descriptions of experimental facts, without the light cast upon them by a theoretical aspect or "explanation" may be desirable, especially in the case of so new a field as colloid chemistry, but does not conduce to the reader's obtaining a lasting familiarity with the matter under discussion.

The suggestion and use of the terms *gelation* (instead of gelatinization) and *to gelate* referring to the formation of gels, and *solation* and *to solate*

referring in the same way to sols, giving the latter a broader meaning than peptization should properly have, seems rather happy.

Although the treatment is at times, especially in the theoretical discussions and the derivation of mathematical formulae, too brief, the book is on the whole by far the most complete and satisfactory that we have in English.

HELEN ISHAM MATTILL.

A Text-book of Dispersoidology (Modern Colloidal Chemistry), in Russian. By A. JANEK. Edited by K. K. Rikker, Morskajor St., Petrograd, Russia. Price, \$1.25.

A short systematic course of Colloidal Chemistry for chemists, physicists, biologists and medical students.

The book contains all of the important material on the subject of Colloidal Chemistry very carefully systematized, with many references and methods, valuable for experimental and research work.

B. R. HONOVSKI.

Publications from the Jefferson Medical College and Hospital. Volume VI. 190 pp. Illustrated. Philadelphia, 1915.

Previous volumes have comprised reprints only, but the present one consists entirely of original papers that have not been and will not be published elsewhere. Although most of the eighteen papers appearing in this volume are of a purely medical nature those listed below contain more or less information of direct interest to the biological chemist.

Osteitis Deformans. A Report of Five Cases with Complete Metabolism Studies in Two Instances and a Review of the Literature. By J. Chalmers DaCosta, M.D., Elmer H. Funk, M.D., Olaf Bergeim, Ph.D., and Philip B. Hawk, Ph.D.

Influence of Anesthesia on the Liver. By John Funke, M.D.

The Effect of an Anesthetic on the Liver. By Melvin A. Saylor, M.D.

Phenolsulphonephthalein Injections for the Estimation of Renal Function. By Alvin E. Siegel, M.D.

A Study of Living Cells on Kinetic and Auxetic Jellies. By J. A. Roddy, M.D., and W. D. Baun.

E. J. CRANE.

A Text-Book of Medical Chemistry and Toxicology. By JAMES W. HOLLAND, M.D. Fourth edition, revised and enlarged. 678 pages, illustrated. Philadelphia and London: W. B. Saunders Company. Cloth, \$3.00.

Earlier editions of this book have been reviewed in the Journal. A review of the third edition is found in Vol. XXXIV, p. 1435. In this edition some new matter has been added, largely in the direction of a discussion of recently described processes in urine and blood analysis. These will be found useful by the classes of medical students for whom the book is intended. The text covers the usual lines included under the general subject of Medical Chemistry.

J. H. LONG.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

THE VALENCE THEORY OF J. STARK FROM A CHEMICAL
STANDPOINT.

Abstracted by DOROTHY A. HARR AND MARY E. HOLMES, by permission of DR. PAUL RUGGLI.¹

Received May 28, 1915.

Since the publication in 1908 of J. Stark's first comprehensive paper "The Valence Theory on an Electroatomic Basis,"² there has been a constantly growing tendency to apply this theory to the interpretation of chemical phenomena. Pauly and Butler have used it to explain the reactivity of the aldehyde group,³ and Ley has followed many of its assumptions in his interpretation of the relation existing between the color and constitution of organic compounds.⁴ A recent treatise by Dr. Paul Ruggli⁵ summarizes the later developments and applications of the theory.

Stark's theory attempts to solve the old problem of valence with the assistance of the new views regarding the atomic nature of electricity.

¹ This manuscript was submitted to Dr. Ruggli and he has kindly suggested some changes, but the manuscript with his revision cannot be passed by the censor at the present time and Dr. Ruggli has very kindly given his consent to publication in the present form. We regret very much that his emendations cannot be secured for inclusion in the review.

² *Jahrb. Radioakt. und Elect.*, 5, 125 (1908).

³ *Ann.*, 303, 254.

⁴ "Farbe und Konstitution bei Organischen Verbindungen," Leipzig, 1911.

⁵ "Die Valenzhypothese von J. Stark von Chemischen Standpunkt," Stuttgart, 1912.

The idea of applying the results of experiments in the field of electricity to chemical problems is not new, but goes back to Berzelius. In more recent times it finds supporters in A. Michael, H. Kauffmann, R. Abegg, W. Nernst, and many others, although it must be added that these names represent a very wide diversity of opinion. Stark seeks to avoid all distinctions between dualistic and unitary views by ascribing the variations (other than size, etc.) between atoms of different elements to a difference in the electric fields of force on the outer surfaces of the atoms. According to the theory, metallic elements appear positive because their atoms easily lose negative electrons, but the same theory makes possible the conception of molecules formed from the same kind of atoms. In general, the hypothesis possesses the advantage of being expressed in a form capable of being put to experimental proof, and has been already partially verified.

The essentials of the electroatomic theory are supplied by the new physical conception of the great difference in volume existing between the positive and negative units of electricity, and by the extended application of the conception of lines of force. The latter idea has been applied already to chemistry in Thiele's "Theory of Partial Valency," and has been helpful in establishing the conception of the divisibility of valence. The theory of partial valency becomes far more valuable when expressed in terms of the electroatomic theory.

The work of Faraday, Helmholtz, and others has established the fact that electricity is not continuous, but has an atomic structure like that of matter. In 1891, J. Stoney suggested the name electron for this "elementar-quantum." As a result of experiments by Helmholtz, Nernst, and Ramsay, we may now picture a negative electron as corresponding roughly in size to a monovalent chemical atom, about $1/1800$ the size of an atom of hydrogen. Similar calculations regarding positive electrical units have not yet been successful, and indeed a positive electron may not even be demonstrated with certainty. Observations up to the present time have merely seemed to indicate that the mass associated with a positive unit of electricity belongs to the same mathematical order as the mass of chemical atoms. (W. Wien, J. Stark, J. J. Thomsen, etc.) This *disparity in size of the negative and the positive "elementar-quantum" is emphasized by Stark.* Regarding negative electrons, it has been demonstrated further that they may be separated from chemical atoms by the expenditure of chemical energy, and that the remaining atom then shows a positive charge.

A close study by chemists and physicists of the association of atoms indicates that the chemical atoms in their combinations do not interpenetrate, but are bound together mainly by their outer surfaces. A conception of the nature of the mutual union of atoms to form molecules

requires an investigation of the structure of the fields of force existing on the outer surfaces of the atoms; and an electroatomic study of chemical action shows that in, or on, the chemical atom positive and negative units of electricity are present as constituent parts. Physicists have even extended these conclusions and advance the hypothesis that the chemical atom is built up of positive and negative units of electricity and of nothing else. This hypothesis is assumed here, but all considerations as to the inner nature of the atom may, for the purposes of the present theory, be disregarded. It is supposed that the surface of a chemical atom may be adequately represented by a three dimensional arrangement of positive and negative electrical charges. If, then, the great difference in size between the fundamental units of positive and negative electricity is considered, the surface of an atom must be pictured as made up of extended zones or spheres (not necessarily spherical in shape) of positive electricity, and between or even above these the comparatively small, point-like, negative electrons. These negative electrons, for reasons which will follow, are to be regarded as valence electrons. Further, since the structure of an electric field is usually represented by the course and density of lines of force which originate at positive charges and end at equally great negative charges, we must imagine a system of lines of force radiating in all directions from the point-like negative electrons, many of them terminating in the extended positive zones on the atom.

The point-like origin and the diverging course of the lines of force are important facts to be remembered in considering the union between one atom and another; for the disparity in the size of the positive and negative units of electricity must be regarded as the determining factor in establishing simple relationships between atoms, such as are expressed, for example, in the fundamental laws of chemistry.

The discrete positive units of electricity situated upon the surfaces of the atoms must not be regarded as consisting of uniformly charged positive zones, but as presenting a concentration of positive electricity at certain points. The neutralizing valence electrons are bound most strongly at these points, and must be assigned, therefore, to quite definite positions on the surface of the atom. If they are pushed from these to neighboring places on the surface, a definite expenditure of energy is necessary. If a valence electron is pushed away from the surface of the atom to a very great distance from it, much more energy must be employed. The maximal amount of this energy measures the strength of the union of the valence electron with the positive sphere of its own atom, and is different for different kinds of chemical atoms. Chemical union between two atoms results because some of the lines of force of a valence electron are detached from its own atom by the approach of the second atom, and become attached to the positive spheres of this atom. In

so far as the negative electrons lying on the surface of the atom exercise those functions of the atom for which chemists have evolved the idea of valency, they may be called valence electrons. In terms of these fundamental conceptions, it is now possible to explain a great variety of individual phenomena.

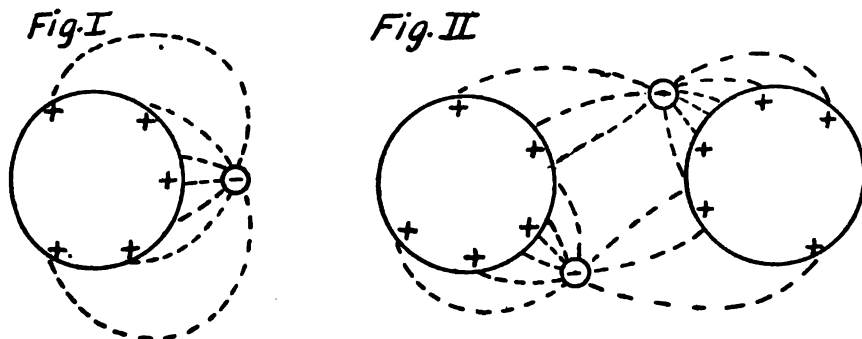
In the static condition the resultant of all the lines of force between the negative electrons and the positive spheres in a compound is zero. If now a part of the system is deflected from its condition of equilibrium, energy is expended against the electric forces and these forces become active as a function of this deviation. Electrical potential energy is in this way created. It reaches the maximum when the individual atoms of the compound become so far separated that the electric force between them becomes very small. On the return of the atoms to the static arrangement these free potential energies, computed at a relatively great distance, are changed into heat, and in this form may be measured. A definite energy value, characteristic of every compound, *viz.*, the heat of formation of that compound, may be, therefore, referred to its dissociated atoms. This potential energy is a minimum in a chemical compound in the static condition. If the same number of chemical atoms is capable of arrangement in different configurations in a molecule, isomeric compounds result, and in such cases several minima are possible. The most stable isomer has a configuration which represents the least potential energy. The heat arising from chemical action may be regarded, therefore, as of electrical origin.

In the act of chemical union between atoms, the negative electron of one atom approaches the positive sphere of another atom, and this is attended by the shortening of the lines of force in the immediate neighborhood of each atom, or, in general, by a contraction of the field of force of the atoms. It therefore follows that chemical reactions are accompanied by changes in volume. This is corroborated by the work of T. W. Richards¹ who has shown experimentally that positive heats of reaction (exothermic reactions) correspond to contractions of volume.

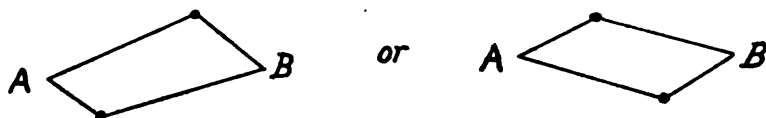
In chemistry it is customary to speak of the saturation or union of valencies. In terms of the electroatomic theory, a valence electron is not bound by another valence electron but by a positive sphere. There are three classes of valence electrons: unsaturated, saturated, and partially dissociated ("gelockert") valence electrons. If a negative electron is bound only to the positive sphere of its own atom, it is called unsaturated, and corresponds to an unsaturated valency in chemical phraseology. Such a condition is represented by Fig. I. By the potential energy, V_u , of an unsaturated valence electron is to be understood the work done when the electron is removed to a relatively great distance from

¹ *Z. physik. Chem.*, 4, 169, 597 (1902).

its position of equilibrium on its atom. Unsaturated valence electrons may appear on single atoms or on atoms that are joined to other atoms. In the latter case more than one electron must be present on each atom. If a valence electron is bound by its lines of force to the positive sphere of another atom as well as to its own atom, it is called saturated. Such a condition is represented by Fig. II. From its nature, a saturated



valence electron appears only in compounds. By the potential energy of a saturated valence electron, V_g , is to be understood the work done when its union with the positive sphere of the second atom is dissolved and the two atoms separated by a relatively great distance from each other. H. Kauffmann has expressed this relation in abbreviated form¹ by the symbols



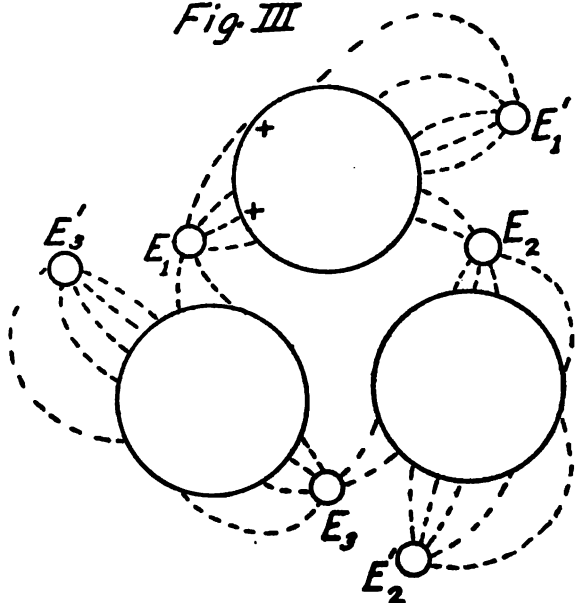
where A and B represent the reacting atoms. The conception of the third class, partially dissociated valence electrons, offers more difficulty because the idea is new. We must imagine an electron that is not bound to a second atom, yet forced away from its own atom. This might be caused by repelling forces, due to the approach of a second atom. Such a condition is represented by Fig. III. This figure shows schematically a compound, consisting of three divalent atoms, on which are present three saturated valence electrons, E_1, E_2, E_3 and three partially dissociated valence electrons, E'_1, E'_2, E'_3 . By the potential energy, V_o , of a partially dissociated valence electron is to be understood the work done when such an electron is removed from its position of equilibrium with relation to its atom to a relatively great distance from its atom. It follows that V_o is smaller than V_u . The unsaturated and the partially dissociated valence electrons may be separated from their atoms in a

¹ *Physik. Z.*, 9, 312 (1908).

compound without destroying the compound. This is not true in the case of saturated valence electrons.

A valence electron bound to only one other atom besides its own represents a condition of *simple saturation*, while an electron bound to two or more other atoms represents a condition of *multiple saturation*. Simple saturation is the more important since it is the condition prevailing in most stable compounds. Under such circumstances the extended positive sphere of an atom, A, must be conceived as occupying a position directly

Fig. III



opposite the valence electron of an atom, B, so that the positive sphere of A receives all the lines of force of the electron that radiate from the side turned away from its own atom. The nearness of the positive and negative charges in such a case make the value V_g of saturation very high, and the union of the two atoms is very stable. The doctrine of valency in chemistry developed from data limited to this simplest type of combination between atoms. The de-

velopment of this doctrine has been attended by many difficulties, among them the application of the conception to molecular compounds. In terms of the theory of valency it is customary to speak of the saturation of valencies and to represent such a condition schematically by a straight line, thus $A-B$, where A and B are monovalent atoms. In terms of the electroatomic theory, saturation implies the union of an electron with the positive sphere of another atom and must be represented schematically by a system of double lines as shown on p. 2615. Such a conception obviates many of the difficulties of the older theory. In terms of it, both molecular compounds and crystalline form may be explained readily by simply extending the idea of multiple saturation. Multiple saturation itself has not been carefully studied because this condition in its very nature implies great instability. Under such circumstances the valence electron of an atom, A, must be imagined as occupying a position opposite two positive spheres of A_2 and A_1 , so that

its lines of force pass simultaneously to the two atoms. It follows that the relatively great extension of the positive spheres hinders any real proximity of the positive charges to the electron attracting them. The value V_g of saturation therefore remains small, and the compound possesses only slight stability. The conception of multiple saturation may be extended to explain molecular compounds by supposing that at one or more points in a stable molecule some of the lines of force, emanating from saturated valence electrons or from positive spheres, may protrude beyond the contour of the molecule. If, now, from some part of a second like or unlike molecule similar lines of force protrude, combination between molecules might result, the positive part of one molecule taking a position opposite the negative part of another and an electrical union taking place. Since only a very small fraction of the lines of force of a saturated valence electron may be imagined as expended in this way, the resulting attraction of the two molecules will be slight. The difference between molecular compounds and crystalline structure is one only of degree. If electric fields of force exist on the surfaces of molecules as well as on the surfaces of the atoms, it may be conceived that, under the influence of these outer fields of electricity, adjacent molecules will seek to orientate in such a way that the negative and positive parts of one molecule shall lie opposite the positive and negative parts of another. If these forces of orientation overbalance in magnitude the energy of the thermic movements of the molecules, there will be established a regular arrangement in the aggregate of molecules, that is to say, crystalline form. In the restricted orientation of positive and negative spheres, within or outside the contour of the molecule, may be found the explanation of varied phenomena—among them the phenomena of tension in Baeyer's sense, and the phenomena of steric hindrance.

Electrical dissociation in metals, gases, and in solution is readily interpreted in terms of the electroatomic theory. It is necessary to distinguish between the movement of ions in solution, of electrons in metals, and of ions and electrons in gases. In all of these cases conceptions are vague regarding the process and the whole matter needs the closest study by both physicists and chemists. Ions may be defined as free moving fundamental units of electricity arising from the separation of electrons from the positive spheres of their atoms. In metallic dissociation, *e. g.*, an unsaturated or partially dissociated valence electron becomes detached from its atom, the residual atom either being isolated or remaining united to other atoms in a molecule. The dissociated electron may remain by itself or may attract to it an electrically neutral atom or molecule. The ease with which dissociation takes place depends upon the relative values of V_u and V_o . If V_u is small as compared with V_o , then even at ordinary temperatures the thermic energy may be sufficient to cause the dissocia-

tion of partially dissociated valence electrons. Equilibrium between the dissociated and undissociated phases depends upon the absolute temperature and upon the relation of V_{∞} to V_0 , the value V_0 being a constitutive property of a compound. In this connection it is interesting to note that saturated compounds of carbon and hydrogen, i. e., the methane and terpene derivatives, show only slight electrical dissociation even at 500° , while benzene, naphthalene, and anthracene, to which on spectro-analytic grounds partially dissociated valence electrons are assigned, show a measurable conductivity, increasing rapidly with increase in temperature. This dissociation is evidently of the same character as that which takes place in metals. Liquid mercury, e. g., shows a noticeable electrical dissociation. It may be therefore multiatomic, with partially dissociated valence electrons. Amorphous carbon shows electrical dissociation while the diamond does not, from which we might infer the presence in the former of partially dissociated valence electrons. It may be added that the heat of combustion of amorphous carbon is greater than that of the diamond.

In electrolytic dissociation it is supposed that the dissociating electron becomes bound to another atom. Ions thus arise, differing as to chemical mass. Their ordered movements, under the influence of the electric current, give rise to the phenomena of electrolysis. In the case of fused salts, it is possible that dissociation limits itself in the sense that the electron of the metallic radical, which is attached also to the metalloid radical, becomes detached *only* from the former without disturbing the integrity of the molecule as a whole. This might happen as a result solely of thermic movements. In the case of dissociation in solution, it is probable that the molecule is broken down, and at the same time the electron of a metallic radical becomes separated from its own radical and attached to the metalloid. Although the reason for this is found in the fact that different chemical atoms bind their electrons with different degrees of force, it is probable that in the case of electrolytes in solution, other factors than thermic movements within the molecule are responsible for the separation. It is likely that the molecules of the solvent enter into reactions with the components of the electrolytes. An *ion* in this case represents a complex formed by components of the dissolved molecule and molecules of the solvent and may be imagined as built up in much the same way as molecular compounds.

The application of the electroatomic theory to phenomena in the field of light is especially interesting, because many of the deductions from theory are here capable of experimental verification. As is well known, a substance is colored if it absorbs light of wave lengths within the limits of the visible spectrum. The light emitted by a colored body may be analyzed by means of a prism and an absorption spectrum may be ob-

tained which is characteristic of the particular substance, and intimately dependent upon its molecular constitution. Since many colorless bodies show light absorption in the ultraviolet and the ultrared, the photographic plate and other devices have been employed, and the absorption spectra of countless chemical compounds have been accurately determined. The application of these results to the determination of the molecular constitution of chemical compounds has been receiving greater and greater attention, especially in the field of organic chemistry, and the question which has arisen as to the cause of the emission and absorption of light has thus come to be of increasing importance. The theory of the electromagnetic origin of light is at present generally accepted, and Stark merely extends this idea when he says that the source of the emission and absorption of light lies in the electrons. As a result of extended experiment it seems probable that the line spectra of the gaseous elements proceed from positive electrical spheres, while the band spectra originate in the movement of negative valence electrons relative to their atoms. The applications of this conception in investigations of the Zeeman effect are interesting. Most striking, however, is the application of the theory to the quantitative determination of the position of the band spectra emanating from (a) unsaturated, (b) saturated, and (c) partially dissociated valence electrons.

(a) Stark calculates the value of the potential energy V_u of unsaturated valence electrons as the product of the electric charge and the ionization tension. Taking the ionization tension as 30 volts, this would bring the lower limit for band spectra of metalloids into the region of the impenetrable ultraviolet, $\lambda = 0.06\mu$. Recent investigations, however, seem to show an agreement even among metalloids of an ionization tension of 6 to 11 volts, which brings the band spectra of unsaturated valence electrons into the region of the ultraviolet. In harmony with these deductions from theory, W. Steubing has found examples of band spectra in the ultraviolet in the case of mercury vapor¹ and also of monatomic oxygen.²

(b) The agreement between fact and theory is even more remarkable, when methods for determining the position of the absorption bands of saturated valence electrons are considered. If the heat of formation of a simple chemical compound has been experimentally determined, it is possible to find the minimal wave lengths of the absorption bands of the substance by the application of Planck's law. Significant calculations have been made in the cases of carbon dioxide and water. If ϵ equals the changed kinetic energy of an electron; c , the velocity of light; λ , the wave length of the emitted radiation, then, according to the fundamental

¹ *Physik. Z.*, 10, 787 (1909).

² *Ann. Physik.*, 33, 553 (1910).

relation discovered by Planck, $\epsilon = \frac{6.55 \times 10^{-27} \times c}{\lambda} = \frac{1.86 \times 10^{-8}}{\lambda}$.¹ If

the quantity of energy capable of being transformed into light is known, a minimal value may be calculated for the emitted wave lengths. Since the emission of band spectra takes place as the result of the fact that the potential energy V_u , V_g , V_o , of an unsaturated, saturated, or partially dissociated valence electron, is changed into radiant energy on the reattachment of the electron to the atom, the value V (V_u , V_g or V_o) may be substituted for the value ϵ in the equation. But since V_g equals the maximal value of potential energy which is never completely transformed into light, the value actually substituted will be smaller than V and, therefore, the true value of λ will be greater than calculated. In other words the observed wave lengths should always be greater (i. e., lie nearer the red) than the wave lengths calculated, and the truth of this has been experimentally demonstrated.

Carbon dioxide may be regarded as a saturated compound. It must then be assumed that in the carbon dioxide molecule the four negative valence electrons of carbon are saturated by the positive zones of oxygen, and the two pairs of valence electrons of oxygen are saturated by the positive zones of carbon. Eight saturated valence electrons are therefore present in a molecule of carbon dioxide. The molecular heat of formation of the substance from isolated atoms is represented by the energy $4n(V_g^C + V_g^O)$, where n equals the number of molecules. For the gram molecule it amounts to 161660 gram calories; for, according to J. Thomsen,² the heat of combustion of isolated carbon equals 135340 and the heat of formation of the oxygen molecule equals 26320 gram calories. If, now, the eight unions are assumed to be equivalent in value, it follows that $nV_g = 20207$ gram calories, $= 20207 \times 4.2 \times 10^7$ ergs per gram molecule. And since a gram molecule at zero degrees and 760 mm. pressure contains

$$n = 1/1.2 \times 10^{-24} \text{ molecules, } \lambda = \frac{1.86 \times 10^{-16}}{20207 \times 4.2 \times 10^7 \times 1.2 \times 10^{-24}} = 1.93 \times$$

10^{-4} cm. $= 1.93 \mu$. Experimental investigation shows that carbon dioxide possesses band spectra, the bands shading toward longer wave lengths, and the edges of the bands having wave lengths $\lambda = 2.6$, $\lambda = 4.3$, $\lambda = 12.5$ – 16μ . When it is remembered that according to Planck's law only a theoretical lower limit for the position of band spectra may be calculated, and that in reality band spectra must lie considerably above this theoretical limit,—the agreement between the observed and calculated values is indeed remarkable. A similar agreement exists between the theoretical and observed values for the position of the absorption bands of water. And since it is probable that the valence electrons contained in water

¹ *Physik. Z.*, 9, 88 (1908).

² *Thermochem. Untersuch.*, IV, pp. 257, 316.

have the greatest energy of combination possible for saturated valence electrons in any compound ($\lambda = 0.73\mu$), it may be suspected that all band spectra of saturated valence electrons lie above the wave lengths $\lambda = 0.5\mu$, that is to say, in the ultrared. If a chemical compound, therefore, possesses a band spectra under $\lambda = 0.5\mu$, the presence of valence electrons other than saturated ones may be inferred.

In the case of saturated valence electrons Stark distinguishes between the bands of total and partial valence fields. The bands of a total valence field correspond to the rotation of the electron as determined by its position in the molecule relative to the positive zones of its own and another atom. Such bands are of short wave length, and lie for the most part in the ultraviolet spectrum. The bands of a partial valence field correspond to the rotation of the electron *together with its atom*, relative to another atom. Such bands are of long wave length and lie in the ultrared. It must be remembered that it is the acceleration of an electron at certain points in its sphere of rotation, that has as its result the emission of electromagnetic waves, in that the kinetic energy of the moving electron is changed into radiant energy. In order to avoid misunderstanding, attention is expressly called to the fact that the band spectra of saturated valence electrons are a constitutive property of the molecule. The band spectra of the same valence electrons of a given atom are, therefore, different in different chemical compounds; and this may be true even if the electrons are bound in these different compounds to the same kind of atoms. If the energy V_g of union is a constitutive property and dependent upon the configuration of the molecule, it follows that the heat of formation or the heat of combustion is also a constitutive property. This has been shown to be the case in a great number of instances—as; for example, the heat of combustion of propylene equals 492700 gram calories, and that of its isomer, trimethylene, equals 499400 gram calories. If, in a series of different compounds, the homologous combinations of the saturated valence electrons present in them are of equal energy values, it follows that the ultrared absorption spectra of these substances are identical. Experimental proof of this is given by J. Thomsen, who shows that the heats of formation of ethane, propane, butane, etc., are compounded additively of the combinations $H \longleftrightarrow C$ and $C \longleftrightarrow C$; and by W. W. Coblentz, who shows that the ultrared absorption spectra of hexane, octane, dodecane, tetracosane, etc., are identical. In the position of the principal bands, ethane and butane agree with them.

(c) It is not possible as yet to make quantitative determinations regarding the spectra of partially dissociated valence electrons. It may, however, be said in general that the potential energy of partially dissociated valence electrons, V_o , is less than the potential energy of unsaturated valence electrons, V_u ; and that, therefore, the band spectra of the former

should lie above greater minimal wave lengths than those of the latter. If the work done on the valence electron in changing it into a partially dissociated valence electron is equal to $a V_u$, where a signifies a number less than unity, then $V_o = V_u (1 - a)$, and accordingly a may be called the coefficient of the partial dissociation of an electron. From this it appears that the band spectra of partially dissociated valence electrons are pushed further towards the ultrared, the greater the value of the coefficient a . Since band spectra of saturated valence electrons lie above $\lambda = 0.5\mu$, the presence of partially dissociated valence electrons must be suspected in the molecule if a substance possesses a band spectra under $\lambda = 0.5\mu$, and if the substance is not known to be unsaturated. For example, benzene is a substance which according to Stark contains partially dissociated valence electrons, since its absorption bands have their edges at $\lambda = 0.233$, $\lambda = 0.268$. According to the electroatomic theory these bands should not be ascribed to the saturated valence electrons which unite C with C, and H with C, thereby holding together the parts of the molecule. If the symbol \longleftrightarrow represents the union of two atoms by means of saturated valence electrons, and the symbol $\text{---}o$ represents a partially dissociated valence electron, then on spectro-analytic grounds the following configurations may be assigned to the benzene molecule. The configuration of Fig. IV is open to the objection that in

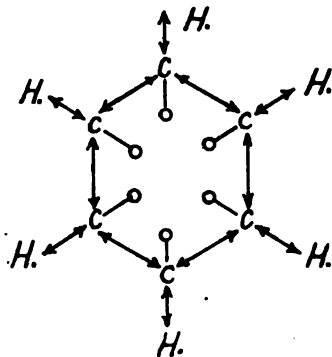


Fig. IV

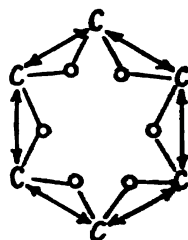


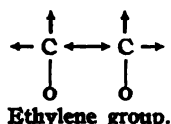
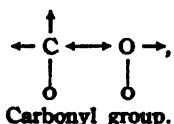
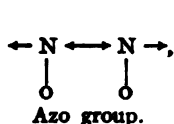
Fig. V

the case of ortho- and meta-substitution products of unlike groups optical isomers are expected. These have been long sought and never found. Kauffmann¹ meets this objection by the configuration represented in Fig. V, which suggests at the same time the formula advanced by Thiele for benzene on the basis of purely chemical investigations. By substitution or condensation the ultraviolet absorption bands of benzene are pushed in the direction of the red, and this, in harmony with the theory,

¹ *Physik. Z.*, 9, 318 (1908).

signifies a decrease in the potential energy of the partially dissociated valence electrons, or an increase in the coefficient of dissociation. If benzene is changed into hexahydrobenzene by the addition of hydrogen, the partially dissociated valence electrons become saturated valence electrons. As is to be expected, the characteristic bands in ultraviolet vanish, and absorption is limited to the ultrared.

The treatment of the chromophore theory and the theory of fluorescence from the standpoint of the electroatomic theory is very important, but can be suggested here only in outline. As is well known, the color in colored bodies is dependent upon the presence in the molecule of certain groups called chromophores. These groups are very reactive and are characterized by the properties of unsaturation. In terms of the present theory, they may be defined as groups that contain at least two multivalent atoms, each possessing a partially dissociated valence electron. Since the band spectra of such electrons lie in the visible or ultraviolet portion of the spectrum, color, in the larger significance of the term, must be associated with these groups; and in this sense, the benzene ring, because of its absorption in the ultraviolet, must be regarded as a chromophore as A. von Baeyer has shown.¹ The electroatomic configuration for benzene has been given: a few configurations for other chromophore groups follow:



The ethylene grouping is particularly interesting because the carbon atoms are not conceived to be joined by a double band, but by means of a saturated valence electron. The presence of a partially dissociated valence electron on each carbon atom conditions the reactivity of the group. Increase in dissociation of valence electrons increases the energy content of the molecule, so that in the case of stereoisomers, the labile form should give an absorption spectrum of the longer wave lengths. This, and other deductions from theory in this field, have received experimental verification. It would be interesting to consider the applications of the electroatomic theory to the phenomena of fluorescence, but this is not possible now for lack of space.

The subject of valency in the Periodic System forms the last topic for discussion. Proceeding from the idea that the forces of affinity or valency are located on the outer surfaces of the atoms, differences of structure must be assumed for the outer surfaces of the atoms of the different elements, depending upon their position in the Periodic System. Certain laws regarding both the value and quality of valency must be noted, in

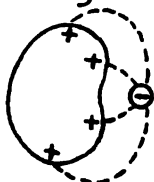
¹ *Z. angew. Chem.*, 19, 1227 (1908).

passing from elements of lower to elements of higher atomic weight. Since one valence electron must be assumed for every valence, the number of such electrons on the upper surfaces of the atoms must be constant for elements grouped together in a vertical series; while in a horizontal series, the number of valence electrons increases by whole units from one to four, and then decreases by whole units to zero. The quality of valency in a vertical series varies in such a way, that the substitution of one element for another in a compound alters the heat of formation of the compound. In terms of the theory the potential energy V_u decreases in any vertical series with increase in atomic weight—that is, the firmness of the union of an electron and its atom is weakened—and this is in harmony with the fact that the electrical dissociation of elements in a vertical series, increases with increase in atomic weight. It may not be decided as yet whether this variation in the strength of union is due to the fact that, with increasing atomic weight, the positive spheres opposite the negative electrons have greater extension, and are therefore a greater distance from the electron; or, whether the positive spheres have almost the same extension, but different inner properties. It should be noted that the strength with which a valence electron is bound to other atoms in the molecule depends not only upon the strength of its union to its own atom, but upon the fact that this union requires a certain volume. This fact alone conditions variations in the quality of valency. Space extension as a property of atoms in a vertical series plays a specially important role in the combinations of multivalent atoms. If a multivalent atom possesses a small volume and, therefore, its valence electrons lie closely together, its union with successive members of another multivalent series becomes more and more difficult, as the atomic weights of these elements increase. It thus becomes evident why, in certain cases, the valency number should not always remain constant in any given vertical series.

As regards variation of the quality of valency along horizontal series, the theory allows of the following interpretation. From one vertical series to another the strength of the union of a valence electron to its atom varies greatly; and for metallic elements in general, V_u is much smaller than for the metalloids. This is in harmony with observations on the ionization of gases. Thus in electrical dissociation electrons separate more readily from a metallic than from a nonmetallic radical, with the result that the one appears with a positive, the other with a negative charge. In passing from one vertical series to the following along a given horizontal series, the distance of the electron from the positive sphere may be imagined to decrease as new material is added to the atoms. It may even be pictured that to the right of carbon, valence electrons become actually embedded in the surfaces of their atoms. This may take place to such a degree that the neutralizing electrons become so deeply

embedded that they no longer emit lines of force beyond the contour of their atoms to other atoms. Figs. VI and VII show atom models

Fig. VI



Monoatomic metal (Na).

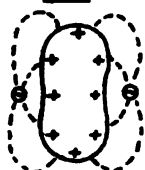
Fig. VII



Monoatomic metalloid (Cl).

as represented in a recent publication.¹ The metal and metalloid elements show great similarity in structure, the difference being in the arrangement of the field of force on their outer surfaces. This conception avoids some of the difficulties of a unitary or a dualistic conception. The protrusion of the negative valence electrons from the surface in the case of the metallic elements, and the receding of valence electrons resulting in corresponding prominence of positive spheres in the case of metalloids, give the character of polarity to the mutual relations of these two groups of elements. Models of multivalent atoms are represented in Figs. VIII to XI. Fig. VIII shows a divalent electropositive atom, as, for example, magnesium; Fig. IX a divalent electronegative atom, as, for example, oxygen; and Fig. X, a trivalent atom, as, for example, nitrogen (the difference in the positions of the electrons may be used to account for the difference between syn- and anti-isomers containing nitrogen).

VIII



IX



X



XI

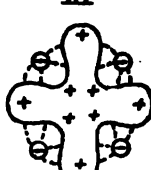


Fig. XI represents the extreme case of an atom, as, for example, of a noble gas, whose valence electrons are so deeply embedded in the positive spheres that their lines of force no longer have the power to unite with the positive spheres of other atoms to form chemical compounds, and the element appears thus to have a valency of zero. Stark has not discussed in this connection the amphoteric element carbon. On the analogy of what has been said, the assumption might be made that the outer surface of this atom presents conditions varying between the electronegative and the electropositive types recalling Michael's phrase "the plasticity of carbon."² Or, there might be a definite arrangement of

¹ *Z. Elektrochem.*, 17, 515 (1911).

² *J. prakt. Chem.*, 60, 325 (1899).

the field of force midway between that of a positive and that of a negative element. The latter view would be in harmony with a continuous transition from the strongly electropositive to the strongly electronegative elements.

This paper can only suggest a few of the applications of the electro-atomic theory of valence. It has been interesting to see the development of the theory during the past six years, to note its constant increase in scope and its ability to harmonize the most varied and complex phenomena in widely separated fields of science. In conclusion it may be said that none of the hypotheses here advanced claims acceptance without further verification. The aim of the theory is to develop gradually a precise and exact conception, which shall meet the fundamental needs of both physicists and chemists, and this end can be attained only by the earnest and critical cooperation of all investigators.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITY AND DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTION.¹

BY CHARLES WATKINS AND HARRY C. JONES.

Received May 29, 1915.

This investigation is a study of the conductivity, temperature coefficients of conductivity and dissociation of electrolytes in aqueous solution. It is a continuation of work begun in this laboratory in 1905,² and which has been continued almost without interruption up to the present.

During the past ten years the following investigations bearing on this general problem have been carried out: Jones and Jacobson,³ Jones and White,⁴ Jones and Clover,⁵ Jones and West,⁶ Jones and Wightman,⁷ Jones and Hosford,⁸ Jones and Winston,⁹ Jones and Wightman,¹⁰ Jones and Springer,¹¹ Jones and Smith,¹² Jones and Howard,¹³ and Jones and

¹ The results of this investigation will appear in full in *Publ. Carnegie Inst. Wash.* No. 230 (1915).

² *Am. Chem. J.*, 34, 357 (1905).

³ *Ibid.*, 40, 355 (1908).

⁴ *Ibid.*, 42, 520 (1909).

⁵ *Ibid.*, 43, 187 (1910).

⁶ *Ibid.*, 44, 508 (1910).

⁷ *Ibid.*, 46, 56 (1911).

⁸ *Ibid.*, 46, 240 (1911).

⁹ *Ibid.*, 46, 368 (1911).

¹⁰ *Ibid.*, 48, 320 (1912).

¹¹ *Ibid.*, 48, 411 (1912).

¹² *Ibid.*, 50, 1 (1913).

¹³ *Ibid.*, 48, 500 (1912).

Shaeffer.¹ Most of the results of these investigations have been recorded in Publication of the Carnegie Institution of Washington, No. 170. For details in connection with the method employed, the above publications must be consulted.

Results.

In the following tables, all conductivities are expressed in Siemen's units, and are molecular conductivities—gram-molecular weights having been used in preparing the solutions. These molecular conductivities (μ_v) were calculated from the equation $\mu_v = Ka V/Rb$; where K is the cell constant, V the volume concentration, R the resistance indicated on the rheostat, (a) and (b) the two arms of the bridge. The percentage dissociation [α] was calculated from the equation $\alpha = 100\mu_v/\mu_\infty$, where μ_∞ is the highest value of μ_v obtained. The temperature coefficients expressed in conductivity units were calculated from the formula

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} = \text{coefficient},$$

in which $(\mu_v)t_2$ represents the value of μ_v at the higher temperature t_2 , and $(\mu_v)t_1$ that at the lower temperature (t_1). These coefficients expressed as percentages were calculated from the formula²

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} \times \frac{100}{(\mu_v)t_1}.$$

For every measurement shown in these tables, three bridge readings involving different values for R were made, and the mean of these readings was taken as the basis of calculation.

Sodium Bromate.—This salt was twice recrystallized and then was dried at 100° for several hours; after cooling over phosphorus pentoxide, the required amount was weighed and put into solution.

TABLE I.

V.	Molecular conductivity.			Percentage dissociation.		
	0°.	15°.	25°.	α 0°.	α 15°.	α 25°.
8	42.77	63.62	78.84	69.9	74.4	74.8
16	44.94	67.03	83.38	73.5	78.4	79.1
32	47.49	70.72	87.95	77.7	82.7	83.5
128	49.64	74.39	92.67	81.2	87.0	88.0
512	52.69	78.76	96.53	86.2	92.1	91.6
1024	53.10	79.59	99.26	86.9	93.1	94.2
2048	58.27	85.45	105.1	95.3	100.0	99.5
4096	61.10	83.34	105.3	100.0	...	100.0

¹ *Am. Chem. J.*, 49, 207 (1913).

² For the temperature coefficients see *Publ. Carnegie Inst. Wash.*, No. 230 (1915).

Sodium Thiocyanate.—The original solution of this salt was standardized by treating a measured volume with a slight excess of an acidified solution of silver nitrate. The precipitate of silver thiocyanate was filtered into a Gooch crucible, washed and weighed. Duplicate determinations were made as in the case of all solutions standardized by analysis.

TABLE II.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	46.79	69.00	84.36	102.5	80.5	79.8	78.2	78.4
8	49.68	72.57	96.36	107.8	85.5	83.9	89.4	82.3
16	50.96	75.86	94.90	114.2	87.7	87.7	88.0	87.4
32	52.90	79.14	98.81	118.6	91.0	91.4	91.6	90.8
128	55.47	83.19	102.8	124.3	95.4	96.1	95.3	95.1
512	57.77	85.81	106.7	129.7	99.4	99.2	99.0	99.3
1024	57.67	86.50	107.8	130.9	99.4	100.0	100.0	100.0
2048	58.10	86.22	107.8	130.6	100.0

Sodium Thiosulfate.—Iodine which had been resublimed in the presence of potassium iodide was weighed into small flasks with tightly-fitting glass stoppers. About 2 g. of potassium iodide and 0.5 cc. of water had been previously weighed into these flasks. After the weight of the added iodine was determined, the flasks were opened in Erlenmeyer flasks containing 200 cc. of water and potassium iodide. This solution was titrated with the thiosulfate. Starch solution was used as the indicator.

TABLE III.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	77.90	115.3	143.3	172.6	59.2	59.1	58.7	59.4
8	82.52	129.8	160.8	196.0	62.8	66.5	65.9	67.4
16	94.10	143.4	178.4	214.8	71.6	73.5	73.1	73.9
32	103.0	153.2	193.0	235.0	78.4	78.5	79.1	80.8
128	113.1	172.4	214.9	259.9	86.0	88.4	88.0	89.4
512	126.0	189.0	234.0	283.8	95.8	96.9	95.9	97.6
1024	124.8	191.9	239.1	284.1	94.9	98.4	97.9	97.7
2048	128.1	194.1	241.1	284.3	97.5	99.5	98.8	97.8
4096	131.4	195.0	244.0	290.5	100.0	100.0	100.0	100.0

Sodium Dithionate.—After recrystallizing from conductivity water, 10 cc. of the sodium dithionate solution was evaporated to dryness in a weighed platinum dish. After heating to a dull red for some time, the dish and contents were cooled over calcium chloride and weighed. From the weight of the sodium sulfate the strength of the original solution of sodium dithionate was calculated.

TABLE IV.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	91.28	135.9	167.8	202.6	65.6	65.2	64.6	64.4
16	99.71	147.6	183.9	220.3	71.6	70.8	70.8	70.1
32	107.8	161.7	200.5	241.6	77.5	77.6	77.3	76.8
128	121.4	180.9	225.0	272.5	87.2	86.8	86.7	86.7
512	130.6	195.6	242.8	293.9	93.8	93.9	93.6	93.5
1024	137.1	203.6	255.0	308.6	98.6	97.7	98.3	98.1
2048	139.1	208.4	259.4	314.3	100.0	100.0	100.0	100.0
4096	139.1	207.3	258.2	312.7

Sodium Pyrophosphate.—This salt was dehydrated and weighed after it had been recrystallized.

TABLE V.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
16	100.2	154.8	194.5	235.3	45.6	44.9	45.3	44.9
32	118.3	181.5	227.5	276.1	53.8	52.6	53.0	52.7
128	159.0	242.7	304.0	370.5	72.3	70.4	70.9	70.8
512	197.0	302.8	384.5	466.7	89.6	87.9	89.7	89.1
1024	211.0	327.0	410.9	508.9	96.0	94.9	95.9	97.2
2048	216.1	336.9	421.8	517.4	98.3	97.7	98.4	98.8
4096	219.7	344.5	428.5	523.4	100.0	100.0	100.0	100.0

Trisodium Phosphate.—All salts of orthophosphoric acid were treated in the same manner. After making a solution of approximately the required strength by weighing the salt, it was standardized by the method of Schmitz.¹ This differs from the usual method, in that the magnesium ammonium phosphate is precipitated in a hot solution, by the slow addition of ammonia to an acid solution of the phosphate, to which an excess of "magnesia mixture" has been previously added. A very pure, coarsely crystalline precipitate, which settles readily, is obtained by this method.

From the weight of the magnesium pyrophosphate yielded by this precipitate on ignition, the strength of the solution of the sodium salt was calculated.

TABLE VI.

V.	Molecular conductivity.			Percentage dissociation.		
	0°.	15°.	25°.	α 0°.	α 15°.	α 25°.
32	120.5	195.3	254.2	61.5	63.6	66.8
128	163.7	261.7	338.1	83.6	85.2	88.8
512	185.2	292.8	361.5	94.6	95.3	95.0
1024	195.8	307.0	380.5	100.0	100.0	100.0

Sodium Dihydrogen Phosphate.—The solution of this salt was standardized by the method discussed in connection with trisodium phosphate.

¹ *Z. anal. Chem.*, 45, 512 (1906).

TABLE VII.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	31.02	47.47	59.79	72.40	72.2	72.4	73.2	71.9
16	33.75	51.62	64.45	79.55	78.5	78.7	78.9	79.0
32	36.16	55.24	69.25	84.25	84.2	84.3	84.8	83.7
128	40.13	60.98	75.39	93.67	93.4	93.0	94.7	93.1
512	43.00	65.52	81.59	99.90	100.0	100.0	100.0	99.3
1024	42.07	64.95	81.17	100.6	100.0

Sodium Tungstate.—The original solution of sodium tungstate was standardized by precipitating the tungstic acid as mercurous tungstate. On ignition this yields the trioxide of tungsten which can be weighed.

TABLE VIII.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	59.56	100.2	54.8	59.9
8	69.75	112.7	141.6	172.0	64.2	67.3	66.9	67.3
16	82.65	126.7	159.0	193.2	76.1	75.7	75.2	75.7
32	87.33	134.3	168.7	205.5	80.6	80.3	79.8	80.5
128	98.54	151.5	190.7	233.5	90.7	90.5	90.2	91.4
512	107.25	164.6	207.4	254.1	98.7	98.3	98.1	99.5
1024	108.67	167.3	211.4	255.2	100.0	100.0	100.0	100.0

Sodium Formate.—In a cold *acid* solution, permanganate acts only slowly with formic acid, while in a hot solution the latter is lost by volatilization. In spite of statements to the contrary, oxidation by means of permanganate in an alkaline solution is a most unsatisfactory process. This led to the use of an indirect method of standardization for the sodium formate solution.

An excess of standard permanganate solution was measured from a buret into an alkaline solution of the formate. After standing for some time, a known weight of pure sodium oxalate was added. The solution was then acidified and heated. A standard solution of permanganate was used to titrate this in the usual way. The total amount of permanganate less that which is equivalent to the sodium oxalate is the permanganate used for the oxidation of the sodium formate.

TABLE IX.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	56.09	84.34	105.0	126.4	70.3	71.0	70.9	68.6
8	62.13	91.91	113.6	140.1	77.9	77.4	76.7	76.0
16	64.75	97.82	121.4	147.4	81.2	82.4	81.9	80.0
32	67.72	99.10	130.2	157.1	84.9	83.5	87.9	85.3
128	72.48	109.8	137.7	166.3	90.9	92.5	92.9	90.3
512	74.63	109.6	139.1	166.7	93.6	92.4	93.9	90.5
1024	75.65	112.8	140.9	181.0	94.8	95.0	95.1	98.3
2048	78.68	114.8	147.9	184.7	98.7	96.7	99.8	100.0
4096	79.73	118.7	148.1	184.1	100.0	100.0	100.0	...

Sodium Chromate.—The original solution of this salt was standardized by precipitating the chromium as mercurous chromate by means of a mercurous nitrate solution. On ignition the mercurous chromate leaves a residue of chromic oxide which can be weighed.

TABLE X.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	74.76	113.4	63.2	64.3
8	83.56	125.3	156.5	187.9	70.6	71.1	71.3	69.6
16	90.74	137.8	171.3	207.6	76.7	78.2	78.0	76.8
32	98.16	148.6	185.1	224.3	82.9	84.3	84.3	83.6
128	110.40	168.4	206.7	252.2	93.3	95.5	94.2	93.4
512	118.32	176.2	219.5	270.1	100.0	100.0	100.0	100.0
1024	114.60	173.6	216.9	262.3

Sodium Dichromate.—The same method of standardization was used in the case of sodium dichromate as was employed with the chromate.

TABLE XI.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	92.18	136.5	87.2	86.22
16	96.57	143.5	176.3	211.4	91.3	90.65	90.71	89.88
32	101.25	148.4	182.7	219.5	95.7	93.74	93.98	93.32
128	106.8	158.3	194.7	233.5	100.0	100.0	100.0	100.0
512	106.1	158.3	194.4	234.6

Potassium Ferricyanide.—This salt was dried for more than a month over phosphorus pentoxide. The solution was prepared by weighing the required amount of the dry salt and dissolving in the usual manner.

TABLE XII.

V.	Molecular conductivity.			
	0°.	15°.	25°.	35°.
8	158.6	230.2	282.1	...
16	168.8	247.3	303.3	360.1
32	181.4	266.4	326.4	389.3
128	207.4	308.2	380.1	451.7
512	229.2	331.8	410.1	494.5
1024	238.1	354.5	438.9	529.9
2048	244.4	363.0	449.5	543.3
4096	254.5	375.3	465.8	564.3

Ammonium Iodate.—A very dilute solution of the iodate, while cold, was carefully treated with sulfurous acid. When an amount sufficient to discharge the brown color due to free iodine had been added, the solution was warmed until the odor of sulfur dioxide could be detected. The iodine was then determined as silver iodide.

TABLE XIII.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
16	48.17	72.21	89.97	108.5	85.1	84.88	84.7	84.4
32	50.51	76.35	94.93	114.6	89.2	89.74	89.4	89.1
128	54.34	81.32	101.1	122.2	96.0	95.59	95.2	95.0
512	56.54	85.07	106.2	128.6	99.9	100.0	100.0	100.0
1024	56.60	84.93	105.9	128.0	100.0
2048	55.99	83.92	104.6	127.2

Monoammonium Phosphate.—This solution was standardized in the same way as described in connection with sodium phosphate.

TABLE XIV.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	37.56	56.27	69.66	83.53	66.4	67.0	66.5	65.9
8	41.18	61.73	76.50	92.71	72.8	73.5	73.1	73.1
16	44.45	66.55	82.57	99.90	78.6	79.3	78.9	78.8
32	46.72	70.65	87.73	106.48	82.6	84.1	83.8	84.0
128	50.74	76.21	94.89	114.75	89.8	90.8	90.7	90.5
512	53.39	81.01	99.73	121.2	94.5	96.5	95.3	95.6
1024	56.50	83.92	104.6	126.7	100.0	100.0	100.0	100.0

Ammonium Chromate.—The method used for standardization was identical with that used for standardizing the chromate of sodium.

TABLE XV.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	93.63	137.0	64.7	64.2
8	102.5	149.8	181.9	215.4	70.8	70.3	69.3	68.8
16	110.5	163.1	199.5	236.7	76.4	76.5	76.0	75.7
32	119.1	176.3	215.4	257.2	82.3	82.7	82.1	82.2
128	135.1	201.2	247.1	292.7	93.4	94.3	94.2	93.6
512	144.6	213.2	262.2	312.7	100.0	100.0	100.0	100.0
1024	143.0	212.6	261.7	312.3

Ammonium Thiocyanate.—The amount of thiocyanate present in the original solution was found by weighing the silver thiocyanate formed on treating a portion of the solution with silver nitrate.

TABLE XVI.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	60.46	86.53	106.0	125.7	83.9	82.2	82.0	81.2
8	61.47	89.84	110.3	131.7	85.3	85.3	85.3	85.0
16	63.58	93.60	114.4	137.5	88.3	88.9	88.5	88.1
32	66.30	97.48	119.5	143.4	92.0	92.6	92.5	92.6
128	68.58	101.2	124.2	148.9	95.2	96.2	96.1	96.2
512	71.74	105.2	129.0	154.5	99.6	100.0	99.8	99.8
1024	72.00	105.2	129.2	154.8	100.0	...	100.0	100.0

Lithium Chromate.—The chromate in this solution was determined as it was in the case of sodium chromate.

TABLE XVII.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	74.62	112.3	139.9	169.1	65.4	67.3	66.9	67.2
16	82.62	124.1	154.3	187.3	72.4	74.3	73.8	74.5
32	89.83	136.6	169.9	205.5	78.7	81.8	81.3	81.7
128	101.6	155.1	193.0	236.5	89.0	92.9	92.3	94.0
512	106.4	164.5	205.3	249.0	93.2	98.5	98.2	99.0
1024	108.1	166.0	206.2	250.3	94.7	99.4	98.6	99.5
2048	114.1	168.3	209.0	251.4	100.0	100.0	100.0	100.0

Rubidium Iodide.—The iodine was determined as silver iodide.

TABLE XVIII.

V.	Molecular conductivity.				Percentage dissociation.			
	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	68.40	97.08	85.41	82.9
8	70.48	101.4	122.6	145.6	88.0	86.6	85.6	85.2
16	72.59	104.3	127.2	150.6	90.6	89.0	88.8	88.1
32	74.75	108.6	131.7	157.8	93.3	92.7	92.0	92.3
128	78.51	114.2	139.7	166.6	98.0	97.5	97.6	97.5
512	79.92	116.0	142.0	169.5	99.0	99.0	99.2	99.2
1024	80.08	117.1	143.1	170.8	100.0	100.0	100.0	100.0

Discussion of Results.

Conductivities.—Electrical conductivity in solutions of electrolytes depends on the number of ions present and on the velocities of these ions. The velocities will depend upon the size and mass of the ions and upon the viscosity of the medium, other conditions being the same. This leads to the conclusion that a salt showing a high conductivity must be dissociated into a great number of ions, or the ions in solutions must be of such a size that they have a great velocity.

It may be seen from the above tables that certain salts, notably trisodium phosphate, sodium pyrophosphate, ammonium chromate and potassium ferricyanide, show very high conductivity. The first of these compounds is strongly hydrolyzed even at low temperatures. The breaking down of complexes by hydrolysis gives rise to a great number of ions also in the case of the pyrophosphate. It is interesting to compare the conductivity of trisodium phosphate with that of the corresponding potassium compound. While both show very high conductivities at all temperatures, the conductivity of the potassium salt is greater than that of the sodium. We would expect this from the fact that the sodium salt crystallized with twelve molecules of water, indicating great hydration in solution; while the potassium salt has no water of crystallization, which indicates only slightly hydrated ions in solution. The am-

ammonium chromate is somewhat similar to the unhydrated potassium salt mentioned above, in that it carries no water of crystallization, and would therefore be expected to show greater conductivity than the corresponding hydrated salts of sodium and lithium. The high values of μ , for potassium ferricyanide are largely due to the great number of ions yielded by this compound. The work of Getman and Bassett,¹ conducted in this laboratory, indicates the production of six ions in solutions of this salt. By comparing the conductivities of the chromates of ammonia and the alkali metals, it is found that they stand in the following order:

Potassium chromate > ammonium chromate >

sodium chromate > lithium chromate

Ammonium compounds, as a rule, show higher conductivity than the corresponding potassium salts. This does not seem to be true in the case of the chromates. The smaller conductivity of lithium compounds, when compared with compounds of sodium, is usually attributed to the greater hydration of the lithium ion in solution, as indicated by the greater tendency of lithium salts to crystallize with water. The chromate of lithium, however, crystallizes with one molecule of water, while the chromate of sodium contains ten molecules. The work of Jones and Bassett² has shown that many substances have greater hydrating power than is indicated by the water of crystallization contained in them. Such may be the case with lithium chromate.

Rubidium iodide shows a higher conductivity than the iodides of the other alkali metals. Knowing that rubidium has a greater atomic volume than sodium or potassium, we might expect the conductivity to be lowered by a decrease in the velocity of the ions, due to their volume and mass. It should be remembered, however, that the hydrating power of these compounds of the alkali metals decreases with increasing atomic volume. Just as sodium salts are less hydrated than lithium, so rubidium compounds would be expected to hydrate less than potassium. Thus, an apparent exception is explained by the theory of hydration.

Dissociations.—As a means of determining the dissociation of salts in solution, the conductivity method is of great service, but it is far from perfect. Hydrolysis, hydration and polymerization all militate against obtaining a true value for μ_{∞} . Since most salts show one or more of the above named phenomena, it is certain that dissociations, calculated from conductivity data, are in most cases simply close approximations.

As a rule, salts in aqueous solutions are more dissociated at low temperatures than at high. This is in accord with the Thomson-Nernst hypothesis connecting dissociating power with the dielectric constant of the solvent. Some exceptions to this rule have been found by other investi-

¹ *Pub. Carnegie Inst. Wash.*, No. 60, 46.

² *Am. Chem. J.*, 33, 562 (1905).

gators. Barium nitrate, cadmium iodide, lead nitrate and uranyl acetate have been found to show an increase in dissociation at higher temperatures. Shaeffer¹ has called special attention to the anomalous behavior of tripotassium phosphate, and suggests, as a cause, abnormal exothermic heat of dissociation. A great number of the substances studied in the present investigation showed a slight decrease in dissociation with rise in temperature. Sodium bromate, sodium thiosulfate, trisodium phosphate and lithium chromate showed a well defined increase. Several compounds showed almost identical dissociation at all the temperatures employed.

Temperature Coefficients.²

It has been found that the increase in conductivity with rise in temperature is due primarily to the velocity with which the ions move. This velocity is governed by the viscosity of the medium and the volume and mass of the ion. It is well known that the general tendency of rise in temperature is to decrease viscosity, and also the volume and mass of the ion; if the ion is considered not as a charged atom or group of atoms, but as a charged nucleus plus molecules of water which must be carried along in all migrations through the remainder of the solvent. Jones has given a number of proofs for the validity of this conception of ions. He has also shown that these complexes break down at higher temperatures. With these facts in mind, we would expect a greater increase in conductivity with rise in temperature in the case of strongly hydrated salts, than in the case of weakly hydrated substances. Taking the amount of water with which a substance crystallizes as indicative of the extent to which it is hydrated, it is found that all of the compounds referred to in the above tables are in accord with this conception, except potassium ferricyanide and ammonium chromate. Reference has been made to the work of Getman and Bassett, which throws some light on the dissociation of the complex ferricyanide, and also shows that water of crystallization is not always indicative of the degree of hydration to which a compound is subject. While they proved that the ferricyanide is not hydrated, it is rather probable that the lithium chromate is, since lithium salts, as a class, have a much greater tendency to hydrate than the salts of sodium or potassium.

The temperature coefficients expressed in per cent. decrease in every case with rise in temperature. They increase somewhat on dilution. This is especially noticeable with hydrated and hydrolyzed salts.

¹ *Am. Chem. J.*, 49, 249 (1913).

² To save space these coefficients are omitted from this paper. They will be recorded in *Pub. Carnegie Inst. Wash.*, No. 230. Some of the relations between them are here referred to.

Jones¹ has pointed out the following general relations deduced from the study of a large number of data concerning temperature coefficients:

1. Those ions with the largest hydrating power have the largest temperature coefficients of conductivity.
2. Those substances having equal hydrating power have approximately the same temperature coefficients of conductivity.
3. At higher dilutions the temperature coefficients of conductivity, for any given substance, are greater than at lower dilutions.

In the present investigation all of these relations have been found to hold, with the few apparent exceptions which are noted in the above discussion.

Summary.

Eighteen more or less unusual salts were studied with reference to the conductivity, over a range of temperature from 0° to 35°, and, wherever possible, their dissociation has been calculated. Their temperature coefficients were also calculated in two sets of units.

The results of this investigation are, for the most part, in accord with the findings of other workers in this field in this laboratory. Three exceptions to the rule that dissociation decreases with increased temperature were found. Two apparent exceptions to the rule that large temperature coefficients are indicative of great hydration were noted, and possible explanations offered.

BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

THE VISCOSITIES OF SOLUTIONS OF CAESIUM SALTS IN MIXED SOLVENTS.²

By P. B. DAVIS AND HARRY C. JONES.

Received August 30, 1915.

Introduction.

We have endeavored for some time to secure enough caesium salts to study their viscosity in pure and in mixed solvents, but only within the past year have we been successful. Through the courtesy of Professor James Lewis Howe, of Washington and Lee University, a quantity of caesium sulfate was placed at our disposal. This was converted first into the hydroxide, then into the carbonate, and finally into the chloride and nitrate; and with these salts this investigation was carried out.

Caesium is the most electropositive of all the elements, and is further distinguished by possessing the largest atomic volume, being followed in

¹ *Am. Chem. J.*, 34, 357 (1905).

² This is part of an investigation which was carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones, and the results will be recorded in full in Publication No. 230 of that Institution.

this respect by rubidium and potassium, respectively. Since salts of the latter two elements are of great interest from the viscosity standpoint, it would be expected that caesium salts would possess, to a more pronounced degree, any peculiarities shown by salts of rubidium and potassium.

An examination of the literature bearing on viscosity shows that, in general, only the salts of the three metals mentioned above are known to lower the viscosity of water. The effect of potassium and rubidium salts on the viscosities of solvents other than water, and of mixtures of such solvents with one another and with water, has been the subject of earlier investigations in this laboratory; and this series of investigations can now be regarded as in a measure completed by the study of caesium salts in these solvents. The present investigation, therefore, has been made to comprise a study of the viscosity of the two caesium salts, chloride and nitrate, in water and in binary mixtures of methyl alcohol, ethyl alcohol, and acetone with water.

The results obtained with caesium salts in formamid as a solvent are now in press,¹ and further investigation of their behavior in glycerol and glycerol-water mixtures, as well as in mixed solvents containing formamid instead of water, is now in progress.

Historical Sketch.

Jones and Linsay,² in their work on binary mixtures of the alcohols with water, found that the molecular conductivities of solutions of salts in these solvents, were, in every case, less than the averages calculated from conductivities in the component solvents themselves. These results, interpreted in the light of the work of Dutoit and Aston, point to a lower degree of association in the case of the mixed solvents than in that of the pure solvents themselves.

Jones and Carroll,³ in extending the above investigation, showed that the change in the viscosity of the medium was an important factor conditioning the decrease in conductivity of salts in such binary mixtures and liquids, the decrease in ionization due to changes in association being only one of the factors to be taken into account.

It, however, remained for Jones and Veazey⁴ to offer a satisfactory explanation of the increase in viscosity which occurs when two highly associated liquids are mixed; and also to account for the phenomenon of negative viscosity, or the lowering of the viscosity of the solvent by a dissolved substance.

¹ *Pub. Carnegie Inst. Wash.*, No. 230 (1915).

² *Am. Chem. J.*, 28, 329 (1902); *Pub. Carnegie Inst. Wash.*, No. 80, 24 (1907).

³ *Am. Chem. J.*, 32, 409 (1904); *Pub. Carnegie Inst. Wash.*, No. 80, 43 (1907).

⁴ *Ibid.*, 107 (1907); *Z. physik. Chem.*, 61, 641 (1908); 62, 44 (1908).

The work of Thorpe and Rodger having shown that viscosities depend largely upon the frictional surfaces of the physical particles in any solution, it followed that if these surfaces were increased or diminished by any means whatsoever, there would result a corresponding increase or decrease in the fluidity of the medium. The work of Jones and Murray¹ had brought out the fact that on mixing two highly associated liquids a material diminution in the association of both takes place. This would result in an increase in the number of ultimate particles in a given volume, with a corresponding decrease in their size, and therefore an increase in their frictional surfaces which would be exposed to one another. Consequently, the viscosity curves for the various mixtures should pass through a maximum, the position of which would depend upon the relative effects of the solvents upon one another.

The reason for the maximum in such viscosity curves and their relation to conductivity having been explained, the effect of certain salts in lowering the viscosity of the solvent remained to be interpreted. Potassium, rubidium and caesium salts, as has already been stated, were known to lower the viscosity of water. These elements occupy the highest maxima on the atomic volume curve, and, as Wagner² had shown, they possess negative viscosity coefficients in water, which vary directly as their volumes. The explanation offered by Jones and Veazey to account for these facts, was that salts of these metals lower the viscosity of the solvent by introducing into it ions which are so large that, when mixed with the molecules of the solvent, they lower the total fractional surfaces exposed to one another. That certain salts of potassium do not produce this effect is due to the fact that the viscosity of the solu-

TABLE I.

Viscosity of Caesium Chloride in Methyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Methyl Alcohol.				50% Methyl Alcohol.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
0.50	0.01674	0.01309	0.01049	0.50	0.02119	0.01547	0.01200
0.25	0.01637	0.01275	0.01021	0.25	0.02084	0.01553	0.01197
0.10	0.01613	0.01243	0.00997	0.10	0.02086	0.01531	0.01179
Solv.	0.01594	0.01235	0.01032	Solv.	0.02100	0.01535	0.01169

25% Methyl Alcohol.				Water.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
0.50	0.01778	0.01338	0.01048	2	0.01098	0.00877	0.0713
0.25	0.01828	0.01360	0.01047	4	0.01111	0.00889	0.0716
0.10	0.01862	0.01358	0.01044	10	0.01133	0.00884	0.0719
Solv.	0.01871	0.01359	0.01032	Solv.	0.01134	0.00891	0.0721

¹ *Am. Chem. J.*, 30, 193 (1903).

² *Z. physik. Chem.*, 46, 867 (1903).

TABLE II.

Viscosity of Caesium Nitrate in Methyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Methyl Alcohol.				50% Methyl Alcohol.			
Viscosities.				Viscosities.			
Mol. conc.	η 15°.	η 25°.	η 35°.	Mol. conc.	η 15°.	η 25°.	η 35°.
2	2
4	4	...	0.01520	0.01177
10	...	0.01244	0.00987	10	0.02072	0.01543	0.01182
Solv.	0.01594	0.01235	0.00978	Solv.	0.02100	0.01535	0.01169

25% Methyl Alcohol.				Water.			
Viscosities.				Viscosities.			
Mol. conc.	η 15°.	η 25°.	η 35°.	Mol. conc.	η 15°.	η 25°.	η 35°.
2	...	0.01300	0.01018	2	0.01075	0.00858	0.00703
4	0.01795	0.01331	0.01028	4	0.01102	0.00871	0.00705
10	0.01832	0.01346	0.01031	10	0.01122	0.00885	0.00720
Solv.	0.01871	0.01359	0.01032	Solv.	0.01134	0.00891	0.00720

TABLE III.

Viscosity of Caesium Chloride in Ethyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Ethyl Alcohol.				50% Ethyl Alcohol.			
Viscosities.				Viscosities.			
Mol. conc.	η 15°.	η 25°.	η 35°.	Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.02777	0.02061	0.01590	2	0.03176	0.02245	0.01635
4	0.02783	0.02039	0.01561	4	0.03346	0.02283	0.01666
10	0.02761	0.01994	0.01500	10	0.03359	0.02274	0.01648
Solv.	0.02762	0.01997	0.01537	Solv.	0.03400	0.02286	0.01618

25% Ethyl Alcohol.				Water.			
Viscosities.				Viscosities.			
Mol. conc.	η 15°.	η 25°.	η 35°.	Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.02381	0.01694	0.01262	2	0.01098	0.0877	0.0713
4	0.02472	0.01738	0.01282	4	0.01111	0.0889	0.0716
10	0.02522	0.01736	0.01276	10	0.01133	0.0884	0.0719
Solv.	0.02585	0.01760	0.01270	Solv.	0.01134	0.0891	0.0720

TABLE IV.

Viscosity of Caesium Nitrate in Ethyl Alcohol-Water Mixtures at 15°, 25°, 35°.

25% Ethyl Alcohol.				Water.			
Viscosities.				Viscosities.			
Mol. conc.	η 15°.	η 25°.	η 35°.	Mol. conc.	η 15°.	η 25°.	η 35°.
2	2	0.01075	0.00858	0.00703
4	0.02424	0.01697	0.01261	4	0.01102	0.00871	0.00705
10	0.02526	0.01745	0.01276	10	0.01122	0.00885	0.00720
Solv.	0.02585	0.01760	0.01270	Solv.	0.01134	0.00891	0.00720

NOTE.—The salt was practically insoluble in the 75% and 50% mixtures.

TABLE V.

Viscosity of Caesium Chloride in Acetone-Water Mixtures at 15°, 25°, 35°.

75% Acetone.				50% Acetone.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
2	2	0.01785	0.01354	0.01060
4	0.01188	0.00930	0.00764	4	0.01783	0.01337	0.01038
10	0.01135	0.00904	0.00740	10	0.01777	0.01316	0.01029
Solv.	0.01125	0.00896	0.00732	Solv.	0.01766	0.01306	0.01009

25% Acetone.				Water.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
2	0.01647	0.01250	0.00983	2	0.01098	0.00877	0.0713
4	0.01667	0.01254	0.00979	4	0.01111	0.00889	0.0716
10	0.01677	0.01246	0.00978	10	0.01133	0.00888	0.0719
Solv.	0.01690	0.01248	0.00964	Solv.	0.01134	0.00891	0.0720

TABLE VI.

Viscosity of Caesium Nitrate in Acetone-Water Mixtures at 15°, 25°, 35°.

75% Acetone.				50% Acetone.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
2	2
4	4	0.01759	0.01320	0.01030
10	0.01143	0.00804	0.00737	10	0.01756	0.01307	0.01017
Solv.	0.01119	0.00878	0.00680	Solv.	0.01767	0.01304	0.01007

25% Acetone.				Water.			
Mol. conc.	Viscosities.			Mol. conc.	Viscosities.		
	η 15°.	η 25°.	η 35°.		η 15°.	η 25°.	η 35°.
2	0.01610	0.01216	0.00965	2	0.01075	0.00858	0.00703
4	0.01655	0.01229	0.00971	4	0.01102	0.00871	0.00705
10	0.01665	0.01244	0.00968	10	0.01122	0.00885	0.00720
Solv.	0.01673	0.01232	0.00962	Solv.	0.01134	0.00891	0.00720

tion is also a function of the anions as well as the cations. When the volume of the anion is very small, the negative effect on viscosity of the cation is more than overcome, and positive viscosity results.

Applying this hypothesis of Jones and Veazey to mixed solvents, Jones and his co-workers have been able to explain a number of facts which otherwise appear to be explicable. For a detailed discussion of this work and a description of the apparatus used in this investigation, consult Publications Nos. 180 and 210 of the Carnegie Institution of Washington.

Discussion of Results.

As can be seen from the tables, measurements have been made of the viscosities of solutions of these salts at 15°, 25°, 35° in mixtures of 25, 50 and 75% of each of the three solvents with water. Caesium salts,

with the possible exception of the carbonate, are practically insoluble in the alcohols and in acetone; and in a number of cases it was impossible to obtain solutions more concentrated than one-fourth normal in the 75% mixtures. In fact, caesium nitrate was not more soluble than tenth-normal in 75% methyl alcohol and 75% acetone, while it is impossible to obtain even that concentration in 75% ethyl alcohol. One peculiarity previously noted in the case of rubidium chloride in 75% acetone was also observed with caesium chloride. A one-half normal concentration of this salt could easily be prepared, but with a partial separation of the acetone from the solvent. However, on cooling below 10° a perfectly homogeneous mixture again resulted, which separated again into two layers on warming. The nitrate at this concentration merely remained partially undissolved. The results obtained are tabulated for each salt, under the heads of the different solvent mixtures, the blank spaces indicating that the salt was insoluble at the concentration in question. In general, both of the salts lower the viscosity of water and of the 25% mixture of all the solvents, and increase the viscosity of the 75% mixture. These facts are in perfect accord with the results obtained in earlier work with salts of potassium and rubidium. In the 50% mixtures the two salts manifest somewhat different behavior. The chloride in 50% methyl alcohol shows an increase in viscosity at all temperatures for the most dilute solutions, and a tendency of the more concentrated solutions to pass over into negative viscosity. The nitrate in the same solvent showed a decided negative viscosity effect.

In 50% ethyl alcohol, a decrease in the viscosity of the solutions as compared with that of the solvent was noted at the lower temperature, a transition to positive viscosity taking place at higher temperatures. Again, the nitrate decreases the viscosity of the solvent at all temperatures.

With regard to the 50% acetone-water mixture, an increase in viscosity at all temperatures is to be noted in the case of the chloride, while the nitrate in this solvent shows a tendency to decrease the viscosity of the solvent, although it increases at the higher temperatures. The difference in the effect produced by these salts, in comparison with that effected by the salts of rubidium, lies in the shifting of the transition point from negative to positive viscosity, towards the mixtures containing the larger percentage of acetone. This follows from the different molecular volumes of the cations of rubidium and caesium. When acetone and water are mixed, the principal changes take place in the association of the acetone. Consequently, until considerable water has been introduced the solvent particles are quite large, so that even caesium nitrate, having the largest negative viscosity coefficient in water, increases the viscosity of the 75% mixture and even of the 50% mixture, except at lower temperatures. For rubidium salts, no examples of negative viscosity are to be noted

until the 37.5% mixture is reached. No data are available for comparison with rubidium salts in alcohol-water mixtures, but it has been shown that potassium iodide increases the viscosity of these mixtures to that concentration containing 40% alcohol. In this instance, however, caesium nitrate decreases the viscosity of the 50% mixture, positive viscosity manifesting itself only in the 75% mixture.

This shifting of the transition point from negative to positive viscosity towards the more concentrated solvents (regarding water as the diluent) with increase in the molecular volume of the salt, brings out clearly the gradual breaking down of the associated molecules into smaller particles with greater fractional surfaces, the difference in the sizes of the particles at different points on the dilution curve, being clearly brought out by the effect produced by salts of differing molecular volumes.

The apparent transition from negative to positive viscosity with rise in temperature, noted in certain instances, would seem to indicate either a polymerization of the salt or else a solvent envelope which is broken down with rise in temperature. Since these salts are the least solvated, the first assumption is apparently the more plausible.

Measurements are now in progress of the effect of these salts on the viscosity of glycerol and of glycerol-water mixtures.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS. PART III.

By J. P. BONARDI AND C. JAMES.

Received October 11, 1915.

This article describes the continued search for a rapid, efficient and economical method for the separation of yttrium from the yttrium earths. All the methods which are herein given are of a fractional precipitation type.

Precipitation by Means of Ammonium Sebacate.—About 12 g. of the mixed oxides were dissolved in dilute nitric acid, diluted to 1200 cc. and made neutral by the addition of ammonium hydroxide. The solution was then boiled and stirred with steam. In order to keep the volume of the liquid in the flask constant, a bunsen burner was always kept going underneath. When the liquid boiled, a 10% solution of ammonium sebacate was added until a fair-sized precipitate had formed. The precipitated sebacates were granular and filtered readily. The filtrate from Fraction I was similarly treated and this was carried out until five fractions were obtained. The various fractions were dissolved in dilute nitric acid, boiled and precipitated with a hot solution of oxalic acid.

The granular oxalates were washed, ignited to constant weight and the equivalent determined as mentioned in Part I.

	1.	2.	3.	4.	5.
Atomic weight.....	97.60	98.00	96.30	94.45	91.70
Weight of fraction.....	7 g.	1.7 g.	2.13 g.	5.23 g.	2.23 g.

A noticeable change of color could be observed in going from Fraction 1, which was light pink, to Fraction 5, which was very pale pink, almost white.

Precipitation by Means of Azobenzene Sulfonic Acid.—A little more than 15 g. of the oxides was dissolved in hydrochloric acid and diluted to 500 cc. The solution was heated to boiling in a beaker, and a hot solution of azobenzene sulfonic acid was slowly added. The azobenzene sulfonates were precipitated from acid solution, and when sufficient had formed it was filtered off and the filtrate treated with more of the reagent. Five fractions were obtained in this way, while a sixth was obtained by the addition of oxalic acid. Since the azobenzene sulfonates are very difficultly soluble even in concentrated acids, the precipitates were decomposed by boiling with sodium hydroxide solution. The resulting hydroxides were dissolved in hydrochloric acid, and the oxalates thrown down by oxalic acid. The colors of the fractions showed practically no change, and the atomic weights given below show that no fractionation took place.

	1.	2.	3.	4.	5.	6.
Atomic weight.....	95.3	95.0	95.0	94.8	94.0	95.2
Weight of fraction.....	0.3 g.	0.6 g.	0.9 g.	1.6 g.	0.5 g.	11.9 g.

Precipitation by Means of Potassium Sulfite.—In this trial, 13 g. of oxide were dissolved in hydrochloric acid, evaporated to dryness, taken up with water, four drops of HCl added, and the whole diluted to 1200 cc. This was brought to boiling and stirred with steam and a 10% solution of potassium sulfite was added drop by drop from a separatory funnel. Four fractions were taken. They were dissolved in dilute HCl, precipitated by oxalic acid, ignited, treated with boiling water to remove any potassium salts, redissolved and converted into the oxalates. The color of the oxides from these fractions varied from pink to very pale pink. The operations were easily carried out, and no difficulty was experienced in filtering.

	1.	2.	3.	4.
Atomic weight.....	97.8	95.8	93.1	92.2
Weight of fraction.....	2.3 g.	5.6 g.	4.3 g.	0.3 g.

Precipitation by Means of Sodium Citrate.—About 15 g. of oxides were dissolved in HCl and made neutral. This was diluted to 1200 cc. and precipitated in a similar manner to the last, with the exception that sodium citrate was used in place of potassium sulfite, and a current of air was used to stir the solution. Four fractions were obtained, and the filtrate

from Fraction 4 was precipitated with oxalic acid. The citrates were ignited to oxide, the latter boiled with water and the oxides reconverted to oxalates. This operation was always carried out whenever sodium or potassium was considered to be present. The color change of the oxide agreed with that of the sulfite method.

	1.	2.	3.	4.	5.
Atomic weight.....	99.8	97.6	95.6	93.4	92.1
Weight of fraction.....	1.1 g.	4.4 g.	3.9 g.	2.8 g.	3.1 g.

Precipitation by Means of Sodium Tungstate.—A dilute solution of the nitrates containing about 12 g. of oxide in 1200 cc. was boiled, stirred and precipitated with a 20% solution of sodium tungstate. The tungstates that were thrown down were very colloidal, and could not be easily filtered. They were allowed to stand overnight to settle and were then decomposed by sodium hydroxide and converted into oxalates.

	1.	2.	3.	4.	5.	6.
Atomic weight.....	96.9	97.7	97.0	96.9	94.4	91.1
Weight of fraction.....	0.12 g.	1.30 g.	1.20 g.	2.20 g.	1.40 g.	3.70 g.

Precipitation by Means of Sodium Tartrate.—Seven grams of the oxides were dissolved in nitric acid and made neutral. The liquid was precipitated at the boiling point with a 20% sodium tartrate.

	1.	2.	3.
Atomic weight.....	98.4	96.1	94.4
Weight of fraction.....	2.1 g.	2.5 g.	2.0 g.

Precipitation by Means of Sodium *m*-Nitrobenzoate.—A solution of 12 g. of the oxides, made similarly to the last test, was diluted to 1200 cc. and fractionally precipitated at the boiling point with sodium *m*-nitrobenzoate. The five fractions obtained showed by color and equivalent determinations that no fractionation had taken place.

Precipitation by Means of Ammonium Camphorate.—Seven grams of oxide were dissolved in nitric acid and made neutral by ammonium hydroxide. The boiling liquid was then precipitated by a solution of ammonium camphorate. The precipitate was very gelatinous and the mass filtered badly.

	1.	2.	3.	4.
Atomic weight.....	95.1	94.8	93.3	93.3
Weight of fraction.....	1.9 g.	1.9 g.	1.3 g.	4.3 g.

Precipitation by Means of Sodium Phenoxyacetate.—Eight grams of oxides were used in this case. The precipitation was carried out in beakers at the boiling point of the solution. The equivalent determination showed that in this case, like the last two, almost no fractionation had taken place.

	1.	2.	3.
Atomic weight.....	95.1	95.1	93.9
Weight of fraction.....	1.4 g.	2.0 g.	5.0 g.

Precipitation by Means of Potassium Cobalticyanide.—About 15 g. of the oxides were dissolved in hydrochloric acid, the solution evaporated

to dryness and taken up with water. The solution was boiled and stirred with steam, while a solution of potassium cobalticyanide was run in slowly by means of a separatory funnel. The cobalticyanides were thrown down in the form of a white, granular precipitate. The liquid filtered easily, and the filtrate was precipitated by oxalic acid. The rare earth cobalticyanide was found to be insoluble in concentrated HCl or HNO₃. However, they were found to be easily attacked by sodium hydroxide. The oxalates that were finally obtained varied very considerably in their color. Fraction 1 was quite pink while Fraction 2 was nearly white. The latter showed only traces of erbium when examined by the spectroscope.

	1.	2.
Atomic weight.....	97.2	91.3
Weight of fraction.....	9.4 g.	4.9 g.

This great difference between two fractions appeared to be very promising and Fraction 1 was run again, and the new first fraction examined with regard to the equivalent. The result showed an atomic weight of about 107, and the oxide itself was of a pale rose color. Since the result was so very good, it was thought best to check it by running a larger quantity of oxide. This time four fractions were obtained by adding potassium cobalticyanide, while the fifth was formed by adding oxalic acid to the filtrate from Fraction 4.

	1.	2.	3.	4.	5.
Atomic weight.....	98.7	95.1	90.8	88.2	90.5
Weight of fraction.....	11.9 g.	11.3 g.	10.4 g.	4.1 g.	0.7 g.

Fraction 5 was interesting because of the high atomic weight. However, the spectroscope showed the presence of neodymium. This fraction, and also Fraction 4, showed an entire absence of erbium bands. The color of the oxides was white, while that of Fraction 1 had a decided pink tint.

This method for the preparation of pure yttrium is without doubt one of the most rapid that the writers have come across. The greatest difficulty consists in controlling the quantity of precipitate.

Further investigations are to be carried on, in the near future, with this very interesting reagent.

DURHAM, N. H.

THE DERIVATIVES OF PERCERIC OXIDE.

[SECOND PAPER.]¹

By C. C. MELOCH.

Received September 13, 1915.

In a previous paper² the author discussed the preparation and properties of perceric potassium carbonate. Special attention was given to the

¹ This paper is based upon part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the degree of Doctor of Philosophy.

² THIS JOURNAL, 37, 2338 (1915).

manner in which the oxygen was combined. Two-thirds of the available oxygen was shown to be peroxide oxygen. The present paper is the result of a series of experiments conducted to investigate the possibility of preparing other perceric derivatives.

Perceric Sodium Carbonate.—Hitherto it has been impossible to prepare the sodium compound by a method analogous to that employed for the preparation of the potassium compound. However, by treatment of the perceric ammonium carbonate solution with solid sodium carbonate in excess and evaporating slowly *in vacuo*, a compound differing in many respects from the potassium compound can be obtained. The crystalline salt is prepared as follows: 26 g. of cerous ammonium nitrate are dissolved in 30 cc. of water and added slowly with stirring to 350 cc. of a saturated solution of ammonium carbonate, to which 10 cc. of 30% hydrogen peroxide have just previously been added. The whole is then agitated in a tall cylinder with a rapid stream of air, or carbon dioxide, until a maximum depth of color is obtained. Three hours' agitation is entirely sufficient. The dark red perceric ammonium carbonate solution thus prepared is then transferred, together with the undissolved portion of the precipitate, to a tall beaker. 200 g. of anhydrous sodium carbonate are then slowly added with constant stirring. The beaker is then placed in a vacuum desiccator containing sulfuric acid in the lower compartment and potassium hydroxide in small dishes in the upper compartment. The mixture is evaporated *in vacuo* at ordinary room temperature until most of the ammonia has been evolved and absorbed. When effervescence ceases in a good vacuum the operation is discontinued. The time required will not ordinarily exceed 48 hours. A pasty mass of sodium carbonate, sodium bicarbonate, sodium nitrate and the perceric sodium compound remains behind. The concentrated solution is filtered through a Büchner funnel and combined with the first extracts. The solid sodium carbonate, etc., is thoroughly mixed with a small portion of water. This solution is conveniently made in a porcelain mortar. The thick paste is then transferred to a Büchner funnel and the extract drawn off. The operations of extracting with a small portion of water and filtering are repeated until the solution obtained is no longer deeply colored. The various extracts are kept separate, or at least only those of approximately the same strength are combined. It is advantageous to start several preparations of the size indicated above and to combine them in the process of extraction. The various extracts are kept at about 5° for at least 48 hours. Usually a crop of crystals will have separated by this time. If the mother liquor be allowed to stand longer another crop will separate especially if a crystal from the first crop is left in the beaker. The first crop is rarely contaminated with solid sodium carbonate, etc., but the last crop usually is. After pouring off the mother liquor it is well to remove

any large crusts of sodium carbonate, etc., that may be present. The crystals are then transferred to a Gooch crucible, or Büchner funnel with fine perforations, and washed with a coarse stream of pure ice water. A good supply of pure ice water, made by letting the wash bottle stand in an ice-salt mixture, should be at all times present in the wash bottle. Mere cold water will not suffice. A strong suction is employed. Neither filter paper nor asbestos are used, since it is necessary that the washing and drying be done rapidly. After the crystals have been washed, the strong suction is continued and the crystals stirred with a glass rod until they no longer adhere to each other or to the stirring rod. When dealing with small quantities it is best to hasten the drying by slipping a cylinder of hardened filter paper down the side walls of the Gooch crucible.

The crystals are sometimes as much as 1 cm. long and 2 to 3 mm. in diameter. The large crystals appear black and the small ones a very deep red. In thin layers the compound is transparent. It is only sparingly soluble in cold water, differing markedly in this respect from the potassium compound, the wash water from which is colored deep red, almost black, while the sodium salt colors the wash water yellow. The sodium compound effloresces in dry air more readily than the potassium compound. Sodium perceric carbonate must therefore be kept in a tightly stoppered bottle. A light brown, opaque compound is formed on efflorescence, which retains the external form of the original crystals. Contact with moisture above 0° causes hydrolysis. The crystals turn a dirty green color. With large quantities of water above 0° the crystals are completely decomposed and a gelatinous, orange-red precipitate is formed.

The compound was analyzed by the methods employed¹ for the analysis of the potassium compound. The results obtained were as follows:

TABLE I.

	I.	II.	III.	Av.	Ratio.		Theoret. comp.
					Det.	Probable.	
Ce.....	19.41%	19.40%	19.44%	19.42%	1.98	2	19.63%
Na ₂ O.....	17.70	17.70	17.71	17.70	4.08	4	17.36
CO ₂	18.41	18.54	...	18.48	6.01	6	18.47
O ²	3.46	3.47	...	3.47	3.10	3	3.36
O ³	3.60	3.63	...	3.59 ⁴	3.21	3	3.36
H ₂ O.....	37.42	37.26	...	37.34	29.62	30	37.82

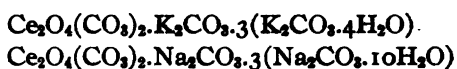
The formula for perceric sodium carbonate is therefore written $\text{Ce}_2\text{O}_4(\text{CO}_3)_{2.4}\text{Na}_2\text{CO}_3 \cdot 30\text{H}_2\text{O}$. An interesting relation, though possibly without significance, is brought out by writing the formulas of the double potassium and sodium compounds as follows:

¹ THIS JOURNAL, 37, 2338 (1915).

² Available oxygen.

³ Unavailable oxygen not otherwise reported determined by difference.

⁴ This value is not an average but is obtained by difference.



Rubidium Perceric Carbonate.—The rubidium perceric carbonate solution was prepared by a method similar to that employed for the preparation of the potassium compound. Owing to the limited supply of material the following modification was adopted: 4 cc. of hydrogen peroxide were mixed with 135 cc. of rubidium carbonate solution which contained about 170 g. of rubidium carbonate. A solution of cerous ammonium nitrate, consisting of 10 g. of the salt dissolved in 15 cc. of water, was added gradually, with stirring. The whole was heated to 60° when almost all of the red-brown precipitate redissolved. The warm solution was chilled almost to 0° and carbon dioxide passed through until a large portion of the rubidium carbonate had been converted to the bicarbonate. The excess of the rubidium bicarbonate was then filtered off by means of a glass wool filter. The remainder of the insoluble material was then removed by filtration through a Büchner funnel provided with a hardened filter, or with a specially prepared asbestos felt. The resulting solution, though very deeply colored, was not sufficiently concentrated to yield crystals on cooling, so that evaporation *in vacuo* over sulfuric acid was required. After some time the solution became sufficiently concentrated to deposit crystals. These crystals were ruby-red in color and closely resembled those of the potassium compound, but have not yet been analyzed.

The rubidium perceric carbonate solution is, if anything, more readily prepared than the corresponding potassium solution and much less readily hydrolyzed. Oxygen is liberated when perceric rubidium carbonate solutions are left in contact with lead dioxide.

Perceric Ammonium Carbonate.—The isomorphism of many ammonium salts with the corresponding potassium salts suggests the possibility of preparing perceric ammonium carbonate. As a matter of fact a perceric ammonium carbonate solution may be prepared by a method analogous to that employed for the preparation of a perceric potassium carbonate solution. The essential difference is that the operation of heating to 60° is omitted. Solution is accomplished by agitation for about three hours with a current of air or of carbon dioxide. The details of the preparation have been given under the preparation of the sodium compound, for which purpose the perceric ammonium carbonate solution can be used to advantage. The last-mentioned solution is less stable than the corresponding solution of the potassium compound, is easily hydrolyzed and decomposes on standing with the formation of a yellow precipitate, presumably ceric carbonate. Although repeated attempts have been made to crystallize out the double ammonium compound by cooling the strong

solution and by slow evaporation *in vacuo* in the cold, such efforts have proven unsuccessful.

Other Perceric Double Carbonates.—The preparation of other perceric carbonates than those of the alkalis presents certain inherent difficulties. Indeed, it is almost certain that the main reason for the fact that double sodium perceric carbonate cannot be prepared by a method analogous to that used for the potassium compound is that the solubility of the sodium carbonate in water at ordinary temperatures is much less than that of potassium carbonate. Another factor possibly is the lesser solubility of the double sodium compound. In order that the double perceric carbonate of a metal may be easily prepared by the above method it seems that the carbonate of that metal must be very soluble. Also, the more electropositive the metal the more easily is the double compound prepared. The method used for the preparation of the sodium compound could probably be used for the preparation of the double perceric carbonates of other metals.

The Preparation of Other Perceric Compounds than the Carbonates.—The substitution of various other acidic elements and radicals for the carbonate groups would seem to be easily accomplished, but, as previously stated, treatment with the mineral acids brings about complete decomposition of the perceric complex. The action of acetic, propionic and butyric acids is somewhat different. Here the solutions that result on neutralization are more or less colored. However, at least partial decomposition takes place, so that the problem cannot be solved in this way.

The possibility of using other readily soluble salts of weak acids instead of potassium carbonate was investigated and, of the salts that were tried, only potassium acetate and magnesium acetate yielded the desired results. The red coloration produced by treating alkaline acetate solutions of cerium with hydrogen peroxide was used by Hartley¹ as a qualitative test for the presence of cerium, but he seems not to have studied the solution quantitatively. The use of hydrogen peroxide and sodium or magnesium acetate as a means of separating cerium from a mixture of rare earths has been studied by Meyer and Koss.² The potassium perceric acetate solution used in the work described below was prepared as follows: 2.5 cc. of 30% hydrogen peroxide are mixed with 100 cc. of saturated potassium acetate solution contained in a small flask. 10 cc. of cerous ammonium nitrate solution, containing about 6.5 g. of the salt, are added slowly with constant stirring. The white precipitate which forms at first is presumably cerous acetate. This precipitate redissolves on rotating the flask and the solution changes from yellow to deep cherry-red

¹ *J. Chem. Soc.*, 41, 203 (1882); *Chem. News*, 45, 40 (1882); *Ber.*, 15, [1] 1439 (1882); *Jahrb. Fortschr. Chem.*, 35, 281 (1882).

² *Ber.*, 35, [1] 673 (1902).

in color. In a short time, in fact almost immediately on warming, a gelatinous red-brown precipitate forms which redissolves on standing, on heating to 60° , or on agitating with a current of air. By these means the excess of hydrogen peroxide is removed and a deep cherry-red solution is obtained identical in appearance with the red solution formed at the beginning, but more stable. It is probable that the excess of hydrogen peroxide is in part, at least, combined with the red-brown insoluble compound which forms, and that this intermediate compound is broken up on agitation, heating to 60° , etc. The red-brown precipitate¹ seems therefore to contain more oxygen than corresponds to the oxide CeO_2 . To obtain the solutions analyzed, the red-brown precipitate was redissolved by heating slowly to 60° and agitating until solution was complete. The red liquid was then cooled rapidly to room temperature.

The ratio of cerium to oxygen in this solution was determined by the following method: 0.7 g. of ferrous ammonium sulfate was placed in a dry titration flask and the air displaced by carbon dioxide. The ferrous sulfate was then dissolved in a minimum amount of cold boiled water. 50 cc. of saturated sodium pyrophosphate were added and the flask shaken until the precipitate which formed at first redissolved. 5 cc. of the perceric potassium acetate solution were mixed with 10 cc. of saturated potassium carbonate solution and added through a dropping funnel. 30 cc. of saturated potassium bicarbonate solution were used to wash the beaker, and were followed by a minimum amount of cold boiled water. The titration of the excess of Mohr's salt was made with potassium permanganate solution as described in a previous paper.²

When 5 cc. of the perceric acetate solution were measured out for the determination of available oxygen a similar portion was also measured out for the determination of the cerium. 5 cc. of concentrated nitric acid were added and the solution evaporated to dryness. In this way most of the acetic acid was removed. The residue was dissolved in water acidified with nitric acid and the cerium precipitated from the boiling solution by the addition of ammonium oxalate solution in slight excess. The cerous oxalate was filtered off, ignited and weighed as CeO_2 .

The ratio calculated from the results obtained from two different perceric potassium acetate solutions was:

Atoms of Ce : Atoms of O (available) : : (I) 2 : 2.66, (II) 2 : 2.67.

The instability of the perceric acetate solution accounts for the difference between these results and the theoretical ratio 2 : 3. An idea of the rate of decomposition is given by the following results obtained from the same solutions one hour later.

Atoms of Ce : Atoms of O (available) : : (I) 2 : 2.51, (II) 2 : 2.45.

¹ Cf. Job, *Ann. chim. phys.*, [7] 20, 261 (1900).

² *Loc. cit.*

The solution of perceric potassium acetate is hydrolyzed by water, liberates iodine from potassium iodide, yields a blood-red solution with potassium carbonate and a red-brown precipitate with hydrogen peroxide. Added to potassium acetate solution containing a little acetic acid, perceric potassium acetate solution is partially decomposed and oxygen is evolved. No success has thus far attended the attempts to crystallize out a double perceric acetate. However, the use of the solution in the preparation of other perceric compounds is quite possible.

The preparation of other perceric acetate solutions than those of the alkalis can probably be accomplished. At any rate, if an attempt be made to prepare perceric magnesium acetate solution by a method analogous to that used for perceric potassium acetate, a blood-red solution is obtained, especially on standing.

Summary.

Perceric sodium carbonate has been prepared for the first time and the rather unusual method of preparation given in detail. The formula is found to be $\text{Ce}_2\text{O}_4(\text{CO}_3)_{2.4}\text{Na}_2\text{CO}_3 \cdot 30\text{H}_2\text{O}$. Although this compound closely resembles the double potassium perceric carbonate in its chemical properties it differs markedly from the latter in physical properties, such as color solubility.

Crystals of the rubidium perceric carbonate have been prepared, but not in sufficient quantity for detailed study. It was observed, however, that they resemble in appearance the corresponding potassium compound.

A method for the preparation of a perceric ammonium carbonate solution has been described and some of its properties studied, but the compound has not been isolated.

The solution prepared by the action of hydrogen peroxide on a cerous salt dissolved in potassium acetate solution has been shown to contain cerium in the perceric form and the important properties of this solution have been described.

The double perceric compounds thus far prepared show the following general characteristics: The metallic constituent other than cerium is a strong base and the acid radical is that of a weak acid. The simple salt which unites with the perceric complex is very soluble. In the cases in which analyses have been made the cerium is in a state of oxidation corresponding to the oxide CeO_2 . Half of the total oxygen combined directly with the cerium is available for wet oxidation under certain restricted conditions. Two-thirds of the total available oxygen is peroxide oxygen.

The facts with regard to perceric compounds are of unusual interest and suggest lines for further investigation. The separation of cerium from thorium has been studied by many chemists. No doubt, perceric compounds present certain possibilities for a new and better solution of this problem. Another problem worthy of investigation is the formation

of double peroxidized compounds of those rare earths which have been shown by Cleve and others to form peroxides. If a number of such compounds could be prepared they would no doubt exhibit a variety in their chemistry sufficient to insure a comparatively rapid and easy separation of at least some members of the rare earth group.

In conclusion, the author wishes to thank Professor Victor Lenher for helpful suggestions and for the interest which he has taken in the above work.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

SOME NEW RARE EARTH COMPOUNDS.

By A. J. GRANT AND C. JAMES.

Received October 11, 1915.

The methods of separation of the rare earths, although greatly improved during recent years, still leave much to be desired. This is especially true of the terbium, dysprosium, holmium portion. Accordingly it seemed advisable to continue the search for suitable compounds either for crystallization or precipitation. Some of the more interesting salts which were prepared, are described below:

Terbium Pyromucate, $\text{Tb}(\text{C}_4\text{H}_7\text{COO})_3 \cdot 5\text{H}_2\text{O}$.—This salt was obtained by neutralizing an aqueous solution of the acid, heated upon the water bath, with terbium hydroxide. In preparing salts of terbium derived from weak acids, it was found necessary to use terbium hydroxide, for the common oxide of terbium is a heavy, dark brown, sometimes almost black, substance very difficultly soluble in acids. When boiled with hydrochloric acid, it showed no signs of dissolving for a long time, but suddenly the whole went into solution.

The solution of the pyromucate was filtered, evaporated and allowed to crystallize. The compound formed radiating crystals, which were very soluble in water.

For analysis, some of the compound was weighed out and ignited to the dark oxide. This dark oxide was then calculated to the white oxide by using a conversion factor, which had previously been determined by a series of experiments in which the dark oxide had been converted to the normal type of oxide by heating in a current of hydrogen. The amount of Tb_2O_3 found indicated that five molecules of water were present. After heating for twelve hours at 94° in a drying oven, nine-tenths of the water was lost.

Terbium 1,2,4-Bromonitrobenzenesulfonate, $\text{Tb}(\text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2 \cdot \text{SO}_3\text{O})_3 \cdot 10\text{H}_2\text{O}$.—This salt was obtained in a similar manner to the pyromucate with the exception that the solution was evaporated to dryness, the residue treated with alcohol and the remaining solid recrystallized from water.

It formed a heavy white compound, made up of very fine crystals. An analysis gave a mean of 15.59% of terbium oxide, while theory demands 15.49%.

The solubility of this bromonitrobenzenesulfonate did not appear to differ much from that of gadolinium. Though these compounds are well defined, they seem to be of no use for separating the rare earths.

Terbium Propionate, $\text{Tb}(\text{C}_2\text{H}_5\text{COO})\text{C} \cdot 2\text{H}_2\text{O}$.—The hydroxide was dissolved in propionic acid until nearly neutral. The filtered solution was evaporated a little, and allowed to cool, when the salt crystallized out. It formed thin, white, powdery, voluminous crystals. The percentage of the normal oxide agreed fairly well with a formula containing two molecules of water of crystallization.

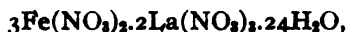
The citraconate and the quinate were found to be very soluble substances.

Caesium Ceric Chloride is a not very stable compound and is formed as follows: A solution of cerous nitrate was precipitated hot by sodium hydroxide and bromine. The ceric hydroxide which was formed was filtered off and carefully washed with water to remove all sodium salts. The ceric hydroxide was suspended in ethyl alcohol and dry HCl gas was passed in while the container was kept cool.¹ The reddish ceric chloride was filtered and mixed with caesium chloride in aqueous alcohol. A yellow precipitate formed immediately. This was separated upon a filter and washed with alcohol. It did not appear to be a definite compound. Ceric chloride also gives a similar derivative with tetramethyl ammonium chloride. This is apparently a little more stable. Ceric pyridine chloride described in the article referred to above is not very definite since the authors obtained material differing in composition by varying the amounts of the reacting salts.

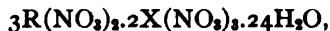
Double Nitrates of the Rare Earths with Ferrous Nitrate.—In order to prepare these compounds, the writers first made a solution of ferrous nitrate by treating ferrous sulfide with nitric acid of a density less than 1.12. The liquid was evaporated below 60°, until green crystals of ferrous nitrate resulted. This very unstable nitrate was dissolved in water and a solution of the required rare earth nitrate added. In the case of the lanthanum double salt, the mixed solutions were placed in a desiccator over sodium hydroxide, and a vacuum maintained until a sufficient amount of lanthanum ferrous nitrate had collected. The flat, green hexagonal crystals were fairly stable in the absence of air. When exposed to the air they slowly turned reddish brown, owing to the formation of a basic ferric salt.

An analysis gave 20.02% La_2O_3 and 14.98% of iron in the form of Fe_2O_3 . This corresponds well with the formula

¹ *Z. anorg. Chem.*, 18, 305 (1898).



or the general type,



where R = Mg, Mn, Co, Ni, Zn or Fe⁺.

Lanthanum Pyromucate, $\text{La}(\text{C}_4\text{H}_5\text{O}.\text{COO})_3 \cdot 2\text{H}_2\text{O}$.—This lanthanum compound separated very easily in the form of crystals from solution in hot water. The results of the analysis of two different preparations indicated the presence of two molecules of water of crystallization.

Yttrium Pyromucate, $\text{Yt}(\text{C}_4\text{H}_5\text{O}.\text{COO})_3 \cdot 3\text{H}_2\text{O}$.—This was prepared in a similar manner to the above. An analysis showed the presence of three molecules of water of crystallization. Upon comparing the amounts of water of crystallization contained by the terbium and yttrium salts, it would seem that more than one state of hydration occurs. These compounds will be studied more completely later on when the writers are able to obtain a larger amount of acid.

DURHAM, N. H.

AN AUTOMATIC VACUUM PUMP.

By OTTO MAASS.

Received September 20, 1915.

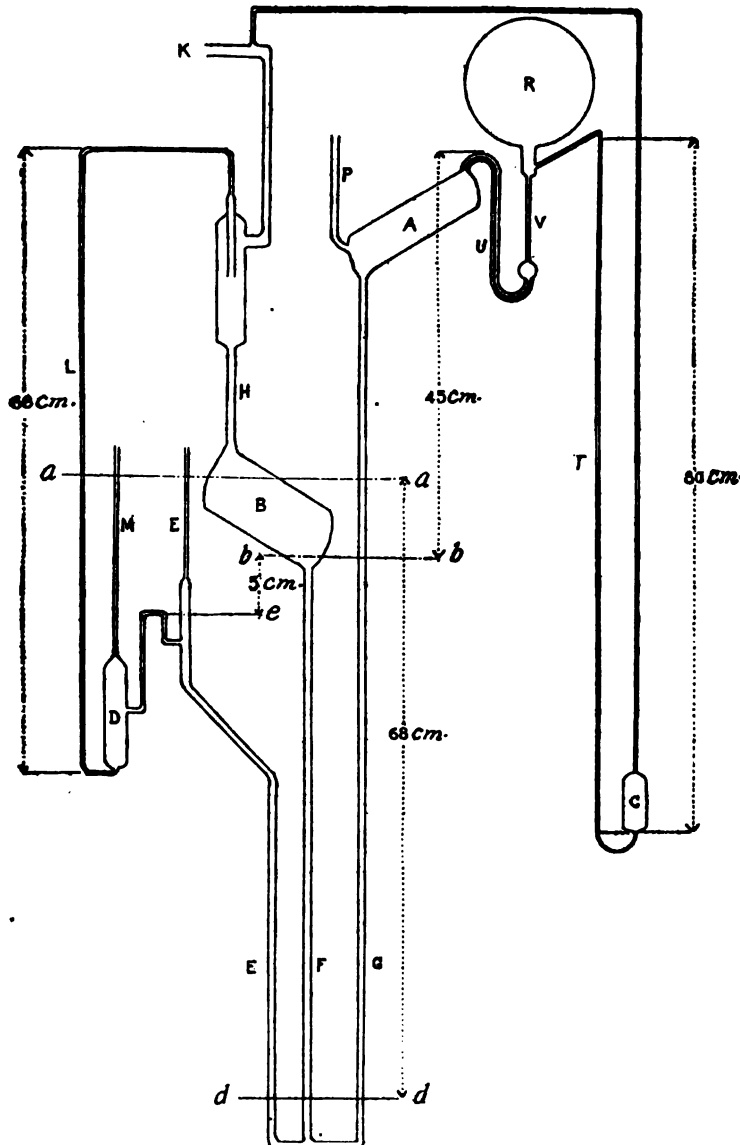
The following is a description of a Töpler¹ vacuum pump which, in conjunction with an aspirator, works automatically. The arrangement does not involve the use of a mechanical spring or valve, is very simple to make, and can, with perfect safety, be allowed to run for an indefinite period.

The diagram shown below has been drawn to scale exhibiting the exact construction of a pump which has been in use for some time.

A is the body of the Töpler pump, tube P leads to the vessel which is to be exhausted, and B is the mercury reservoir. At the start, when the air throughout the apparatus is at atmospheric pressure, the mercury stands at level *a* in B and also in tubes M, E, L, and G. Tube K leads to the water pump. When the latter is set in action air is drawn out of A, P and R through one centimeter of mercury in bulb C and out at K. Simultaneously the pressure over the mercury in B is diminished, so that, since tubes E and M are open to the air pressure, the mercury level will be lowered in these. The volume of B being large compared to the volume of the tubing, the mercury gradually drops to the level *d* in tube E while the mercury rises to the top of tube L. A further decrease in the pressure and the mercury in the bottom of bulb D is forced through L, and runs down H into B. Air now enters tube M into the water pump and into B and C, where the pressure is now that of the outside atmosphere. The mercury in bulb C rises in tube T so that the pressure in A remains equal

¹ With Antropoff modification, *Chem. Ztg.*, 34, 979 (1910).

to that pressure to which it had been reduced by the water pump. Therefore the atmospheric pressure acting on the mercury in B forces the latter into A, the air in A being forced into R through capillary tube U. At the same time the mercury rises in tube E, fast at first, but then more slowly, until it rises at the same rate that the mercury rises in A. Finally when the mercury in A reaches the capillary tube the mercury in E rushes up to level *b* to which level the mercury in B has fallen. In passing the



level e mercury flows into bulb D, preventing further access of air to the water pump. The pressure in B immediately decreases so that the mercury is drawn back from A, which latter is now cut off from R by mercury in the capillary tube U. Simultaneously the mercury level in E is lowered below level e , and the mercury rising in tube L is finally forced into B so that the atmospheric pressure again presses on the mercury in B. The volume of R is larger than that of A, so that the air forced out of A into R does not increase the pressure in the latter to any great extent. In each cycle, when the pressure over C is decreased sufficiently, air is drawn out of R, so that the pressure in the latter always falls short of the column of mercury in capillary tube U. Each time that mercury is driven through the capillary tube it rises in V, out of which it is forced back into A when the mercury is leaving the latter, the difference in level of the mercury in U and in V becoming equal to the pressure in R. It is essential that tube G be connected to tube F at the same level that E is joined to F.

It was found to be serviceable to join the ends of tubes M and E to a common glass tap. This was closed at the start, enabling a thorough preliminary exhaustion by means of the water pump. Then, on opening the tap, air can enter M and E and the pump starts working. This saves a little time. Furthermore it is advantageous to have a tube and a glass tap attached near the top of tube T. This enables one to let air into the apparatus at the end of an experiment. These taps have not been included in the diagram since they are not necessary to the running of the pump, but are simply added conveniences.

The pump was found to work rapidly after the first exhaustion; it is possible to have two complete cycles occur in one minute.

That portion of the pump which has to do with the ejection of the air forced out of A is similar to an arrangement previously described in *THE JOURNAL*.¹ Otherwise, as far as is known to the author, the device is new.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

ELECTRICAL TRANSFERENCE IN AMALGAMS.

BY GILBERT N. LEWIS, ELLIOT Q. ADAMS AND EDITH H. LANMAN.

Received October 2, 1915.

According to the electron theory, electrical conductivity of a metal is assumed to be due almost solely to the passage of the negative electron through the body of the metal. Although the mobility of the free electron is doubtless far greater than that of any other carrier, still the other substances carrying electric charges are acted upon by the same forces which cause the motion of the electron and, having a finite mobility,

¹ F. M. G. Johnson, *THIS JOURNAL*, 34, 909 (1912).

must take a certain part in electrical conduction. In the case of a pure metal it is hard to see how any experiments could be designed for the study of that part of the conduction due to these other carriers. But in the case of a solution of one metal in another it seemed not improbable that the passage of a heavy current for a number of days might result in appreciable concentration changes at the electrodes.

When a metal is dissolved in a nonmetallic solvent, as sodium in liquid ammonia, it dissociates, according to the well-substantiated theory of Kraus,¹ into a positive ion (sodium ion) and negative electrons, which may be in part combined with the molecules of the solvent. When an electric current is passed through such a solution, the dissolved metal is carried with the positive current. According to the prevalent theory of metals it seemed not unreasonable to expect that a highly electro-positive metal, such as sodium, when dissolved in a far less positive metal, like mercury, would behave in a like manner. We were therefore at first surprised by the results of the experiments which we are about to describe and which show definitely that in both sodium and potassium amalgams there is in fact a change of concentration accompanying the passage of electricity, but that the dissolved metals travel with the negative current.

Preparation of Amalgams, and Transference Apparatus.

Sodium and potassium amalgams were prepared by electrolysis of concentrated solutions of the respective hydroxides with a cathode of pure mercury. The amalgams were transferred to evacuated glass containers equipped with vacuum stopcocks. After thorough shaking the container was sealed to the transference apparatus as shown in Fig. 1. H is the amalgam reservoir and ACB is a glass tube, 2 mm. in bore and 20 cm. in length. Stout, platinum electrodes are sealed in at A and B. In the first experiments, stopcocks below A and B permitted the withdrawal of amalgam from the two limbs. This method was later discarded, owing in part to the danger of contamination of the amalgam by the stopcock lubricant and in part to the difficulty of removing the last traces of adsorbed water which, clinging tenaciously to the walls of the glass tube, reacted with the amalgam, forming numerous small bubbles of hydrogen. In the later form of apparatus, shown in the figure, the whole tube up to E could be heated in an oil bath to over 200° while the apparatus was exhausted to 0.1 micron of mercury through F. After cooling the

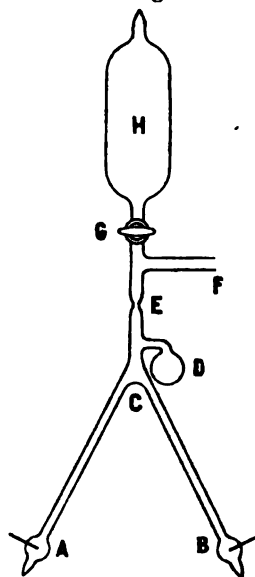


Fig. 1.

¹ Kraus, *THIS JOURNAL*, 30, 1323 (1908).

apparatus, the amalgam was allowed to enter through stopcock G and the transference apparatus, sealed off at E, was ready for use. A current of 4 to 8 amperes was allowed to run several days so as to give approximately 1000 ampere hours. The current was read with an ammeter. Minor uncertainties, owing to fluctuations, and in one or two cases to actual cessation of the current, were negligible compared with other experimental errors.

In order to prevent convection of amalgam, it seemed advisable not to attempt to maintain constant temperature throughout, but rather to establish a temperature gradient from the upper to the lower portions of the apparatus, so that the density increased gradually from top to bottom. This was accomplished by encasing the tube, at the bend C, in asbestos, thus retarding the escape of the heat generated by the current.

At the conclusion of the experiment the apparatus was tipped so that the amalgam in the tube at C flowed into the empty bulb D. The two limbs were sealed off and their contents were weighed and then analyzed by treating the amalgam with a slight excess of standardized hydrochloric acid (0.2 *M*), measured from a weight buret, the residual acid being titrated back with carbonate-free sodium hydroxide (0.01 *M*). The method of procedure will be described in the next section.

An Improved Procedure for Alkalimetric Titration.

Since the portions of amalgam which were analyzed contained but small quantities of dissolved metal (from 0.3 to 4 milli-equivalents), the determination of the small changes in these quantities, due to the passage of the current, was a matter of some difficulty. The ordinary methods of alkalimetric titration are open to criticism, owing to an improper choice of indicator and to the absorption of carbon dioxide from the air. Especially when titrating small amounts of dilute acid and alkali, it is important that the indicator should change color rapidly through a small range of hydrogen ion concentration and that the point of maximum color change should be near the neutral point. An investigation of a number of the common indicators has convinced us that rosolic acid best satisfies these conditions. The color change occurs almost at the point of equal hydrogen and hydroxyl ion concentration, and 0.01 cc. of 0.01 *M* alkali produces a marked change of color in a total volume of 20 cc. This indicator unfortunately fades appreciably in the course of a few minutes, but this difficulty may be overcome by adding only a part of the indicator at first and the remainder when the titration is nearly at an end.

The titration was carried out in narrow flat-bottomed cylinders which were carefully steamed (a high grade of resistance glass would be preferable). When only a slight excess of acid remained a stream of air, freed from carbon dioxide by soda-lime, was led through a glass tube into the solution. This not only effectively stirs the solution, but in the

course of five minutes completely sweeps out whatever carbon dioxide may be dissolved. The end point is then very sharply obtained.

The whole procedure is extremely simple and satisfactory, and such discrepancies as are to be observed in the tables given below are to be attributed not to the analytical method, but rather to the difficulty of dealing with so reactive a substance as sodium or potassium amalgam.

Results of the Transference Experiments.

Our experiments show definitely that both sodium and potassium dissolved in mercury are transferred from one electrode to the other during the passage of a current and that both are carried with the negative current.

Table I gives the results of three experiments with sodium amalgam which had, according to three analyses (average deviation from mean 0.05%), 3.240 atom per cent. of sodium. The first column gives the number of grams of amalgam, respectively, in the anode and cathode portions; the second, the number of milli-equivalents of sodium originally contained in these portions; the third, the increase in the number of milli-equivalents in these portions accompanying the passage of the quantity of electricity given in column four. The fifth column shows the number of equivalents transferred per faraday, namely, the ordinary transference number, together with the mean of the transference numbers obtained from the anode and cathode portions. It is to be noted that this mean may be calculated without any knowledge of the original composition of the amalgam.

TABLE I.

	Wt. of each portion.	Milli-equiv. Na (orig.).	Incr. in milli-equiv. Na.	No. of ampere hrs.	Transference number $\times 10^4$.
a.....	24.072	4.112	0.152	600	6.78
c.....	25.684	4.387	-0.025	..	1.10
					Mean, 3.94
a.....	9.588	1.638	0.098	850	3.08
c.....	8.421	1.439	-0.066	..	2.08
					Mean, 2.58
a.....	9.566	1.634	0.093	1250	1.99
c.....	8.368	1.429	-0.118	..	2.53
					Mean, 2.26
					Average, 2.93

Whatever theory we may offer for the mechanism of this transference, we should expect that in very dilute amalgams, where the conductivity does not differ materially from that of pure mercury, the amount of sodium transferred per faraday would be proportional to the concentration of sodium in the amalgam, and even at such concentrations as are here employed we might predict that this would still be approximately true. A few measurements were made with sodium amalgam, 0.577 atom per cent. (average of four analyses, average deviation 0.4%). Owing to the

very small amount of sodium in the electrode portions, these measurements were extremely difficult, but we believe we may rely upon the approximate validity of the three results which were obtained and are given in Table II, in which the several columns have the same significance as in Table I. The anode portion of the second run was lost.

TABLE II.

	Wt. of each portion.	Milli-equiv. Na (orig.).	Incr. in milli-equiv. Na.	No. of ampere hrs.	Transference number $\times 10^4$.
a.....	26.384	0.7610	0.0126	1035	0.325
c.....	20.468	0.5804	-0.0134	..	0.347
					(Mean, 0.336)
c.....	25.352	0.7308	-0.0063	805	0.211
					Average, 0.294

The ratios of transference number to atom fraction from Tables I and II, respectively, are $2.93 \times 10^{-8}/0.0324 = 0.90 \times 10^{-4}$; $0.294 \times 10^{-8}/0.00577 = 0.51 \times 10^{-4}$. The difference between these two numbers is barely within the limits of probable experimental error.

The next experiments were made with potassium amalgam, 2.1604 atom per cent. (two analyses, average deviation 0.04%). The results are given in Table III.

TABLE III.

	Wt. of each portion.	Milli-equiv. K (orig.).	Incr. in milli-equiv. K.	No. of ampere hrs.	Transference number $\times 10^4$.
a.....	10.963	1.205	0.173	1250	3.72
c.....	10.447	1.148	-0.177	..	3.80
					Mean, 3.76
a.....	10.892	1.197	0.042	1000	1.13
c.....	9.087	0.999	-0.239	..	6.40
					Mean, 3.76
a.....	13.601	1.495	0.191	2000	2.56
c.....	17.274	1.899	0.283	..	3.79
					Mean, 3.17
					Average, 3.56

Since these measurements were made, it has seemed not unlikely that in spite of repeated shaking the amalgam may not have reached complete uniformity of concentration. The mean of transference numbers from anode and cathode portions of each run can be obtained without a knowledge of the original composition. The three results so obtained show an average deviation from the mean of only 7%. Dividing the average transference number, 3.56×10^{-8} , by the atom fraction, 0.0216, gives 1.65×10^{-4} , which is about twice the corresponding number for sodium.

Theoretical Considerations.

A clue to the interpretation of this apparently mysterious transference effect in amalgams is found when we examine the curves relating the

electrical conductivity and the composition of liquid amalgams of sodium and potassium. Bornemann and Müller¹ have shown that the electrical conductivity of mercury is lowered by the addition of sodium.

Now, unless the sodium diminishes the number of electrons which take part in the conduction, which seems improbable, this change of conductivity must be due to a diminution in the average mobility of the electrons. Probably the atoms of sodium which are dissolved in mercury are not there chiefly as such, but rather as nuclei of large aggregates of mercury atoms. Be this as it may, we can consider a dilute amalgam as composed of small regions whose centers are the sodium atoms, embedded in a mass which has all the properties of pure mercury. If an electron meeting one of these regions during the passage of the current is on the average retarded, whether by the greater impenetrability of that region or by any kind of reflection or refraction, then, by the law of action and reaction, the region containing the sodium atom will be impelled in the direction of the negative current.

This was the explanation of our results which we adopted before the experiments with potassium were made, and on the basis of this explanation we predicted that a similar amalgam, which at the same equivalent concentration shows a greater effect than that of sodium in diminishing the conductivity of mercury, would have a larger transference number than that found for sodium amalgam. Bornemann and Müller have shown that potassium, in its dilute amalgams, lowers the conductivity of mercury about twice as much as an equivalent amount of sodium, and the fact that our potassium amalgams gave twice as great a transference number as sodium amalgams at the same concentration is a striking corroboration of the explanation which we have offered.

In order to establish a quantitative relationship between the electrical conductivity and the transference number of amalgams, it would be necessary to consider the mobility of the solute as shown by measurements of the diffusion coefficient. Without entering into a further discussion of this point at the present, we may nevertheless call attention to one simple corollary of our theory, namely, that a dilute amalgam which has the same electrical conductivity as pure mercury would show no electrical transference.

Certain metals like lithium and calcium increase the conductivity of mercury² and it will be very interesting to see whether these amalgams show, as our theory would predict, a transference in the opposite direction to that of potassium and sodium.

In conclusion we may point out an interesting thermodynamic consequence of the electrical transference. It is commonly stated that a

¹ *Metallurgie*, 7, 396 (1910).

² Bornemann and Rauschenplat, *Metallurgie*, 9, 505 (1912).

completely metallic circuit, all at one temperature, can give no electromotive force. This is a thermodynamic necessity if there is no process accompanying the passage of a current, except the absorption of heat from the surroundings, which could serve as a source for the electric work. We may, however, construct a new type of concentration cell, composed entirely of metals, which, according to the results of our transference experiments, should give a definite and measurable electromotive force. If we have in contact with one another two sodium amalgams of different concentrations and a platinum electrode in each, we may expect to obtain an electromotive force between the electrodes, owing to the fact that a current passing through such a cell in the right direction will carry the sodium from a region of higher to one of lower concentration. Experiments with such concentration cells are now in progress, and may afford a more exact method of determining the transference number of amalgams.

Summary.

An electric current passing through a dilute amalgam of sodium or potassium causes a transfer of the dissolved metal in the direction of the negative current. The number of equivalents carried per faraday is 2.9×10^{-6} in sodium amalgam of 3.24 atom per cent., and 0.29×10^{-4} in sodium amalgam of 0.577 atom per cent. In potassium amalgam of 2.16 atom per cent. it is 3.6×10^{-6} . An explanation of this transference is offered and the relationship between transference number and electrical conductivity is pointed out.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON.]

MOLECULAR WEIGHTS OF GASES BY AN EVAPORATION METHOD.

By H. L. TRUMBULL.

Received September 27, 1915.

Before the researches of Stefan¹ on the rates of evaporation of ether and carbon disulfide into different gases, it was generally believed by physicists that the rate of evaporation of a liquid is independent of the character of the gas above the liquid.² Stefan demonstrated that the velocity of evaporation varies with the nature of the gas above the liquid,

¹ M. J. Stefan, *Wien. Akad. Ber. Math. Naturw.*, 68, 385 (1872). See also *Ibid.*, 63, 163 (1871) and 65, 323 (1872).

² Stefan quotes from Marbach's *physikalischen Lexicon* under the heading "Verdunstung und Verdampfung," as follows: "Die Natur der Luftarten übt übrigens keinen Einfluss auf die Verdunstung der Flüssigkeiten, sobald nur die Umstände also der Druck, die Temperatur u. s. w. gleich sind. Mag die Verdunstung in einer Atmosphäre von Sauerstoff, Wasserstoff, Stickstoff, Kohlensäure, oder an der Luft selbst, vor sich gehen, die Menge der entweichenden Dämpfe bleibt sich bei den

and established four laws for the process. His apparatus consisted of capillary tubes of 0.6 to 6.0 mm. bore, and of several centimeters length, filled with ether, and exposed to the air of a room near an open window. No thermostat was employed, and the amount of evaporation was measured by reading the loss in height of the liquid column after a given interval of time.

Stefan did not employ water in his investigation, owing to its slow rate of evaporation and to the variable humidity of atmospheric air, for which it would be difficult to make corrections. He was able to connect the rate of evaporation with the dimensions of the capillary, the temperature, and the vapor pressure of the liquid under consideration. It remained for Winckelmann¹ and Guglielmo² to extend the measurements to include water as well as other liquids. The apparatus of the former consisted of a small test tube fitting snugly into a hole in the bottom of a larger one. The liquid was contained in the smaller test tube and the gas employed was supplied at high velocities by means of a glass tube terminating just at the mouth of the lower test tube. The larger test tube was thus filled with pure gas throughout the course of the experiment. The loss by evaporation was measured by reading the heights of liquid before and after a given time interval.

Winckelmann observed that for many liquids the rates of evaporation depended upon the gas used, being most rapid for hydrogen, and correspondingly slower for the heavier gases. He also calculated diffusion coefficients for the various pairs of substances investigated. The objection to Winckelmann's method is that he used a blast of air, which is not permissible in the measurements of the free diffusion of gases.

Recently P. Vaillant³ has made use of an evaporation method to measure the vapor pressures of solutions. His method is interesting in that it employs a weight-loss rather than a volume-loss method of measuring the amount of evaporation. It is not, however, free from objection, since his loss in weight was invariably less than one milligram.

The object of this investigation was to find a simple and accurate method for the measurement of rates of evaporation of water into different gases, with a view to ascertaining the relation between the rates and the densities of the gases used. The first requirement of the method was that it should eliminate the objections involved in the preceding investigations and provide a perfectly dry atmosphere, immovable, and at a constant

einzelnen Flüssigkeiten, sobald sich die Bedingungen unter denen die Verdunstung stattfindet nicht ändern, gleich. Das ist schon in früherer Zeit durch Volta, Saussure, Dalton, De Luc, und Clement und Desormes nachgewiesen."

¹ Winckelmann, *Ann. Phys. (Wied.)*, 22, 159 (1884).

² Guglielmo, *Beibl.*, 8, 20 (1884).

³ P. Vaillant, *Compt. rend.*, 148, 1099 (1909); see also, W. Müller Hrbach, *Sitzber. K. akad. Wiss. (Vienna) Math. Naturw. Kl.*, 112 (pt. 2a), 615 (1903).

temperature, and that the loss by evaporation should be measured by a weight-loss method and not by a volume-loss method. Water, rather than another liquid, was chosen because of the greater interest attaching to evaporation studies in which water is involved.¹

The apparatus employed in this investigation was very simple. It consisted of a small (3 cc.) flask evaporator, made from 1 to 6 mm. tubing and provided with a glass stopper. This flask contained water, saturated with the gas used. The dry gas was contained in an Erlenmeyer flask in contact with phosphorus pentoxide. At the beginning of an experiment the evaporator was connected with the flask and the whole apparatus was immersed in the thermostat at $25.07^\circ \pm 0.01^\circ$. After several days the apparatus was removed, and the weight of liquid lost from the evaporator, determined. This weight loss divided by the time in hours and multiplied by the barometric height in mm. gives the value for the constant (Col. 5) in the tables. This constant is derived on the basis of the law first formulated by Dalton² that the rate of evaporation is directly proportional to the aqueous tension of the liquid and inversely proportional to the atmospheric pressure. For slight differences in barometric height the law of Dalton gives values for the evaporation constant which agree with each other fully as well as those, calculated on the basis of Stefan's law,³ viz.: $dW/dt = K \log B/B - p$, where B is the barometer reading and p is the vapor tension of the liquid.⁴

Theoretical.—Let us try to picture to ourselves the mechanism by which evaporation takes place from the surface of a pure liquid into an infinite atmosphere of dry gas. At the surface of the liquid, we have a saturated vapor in equilibrium with the liquid. The vapor pressure of the superambient atmosphere is maintained constantly less than at the surface, being of course nil in a perfectly dry atmosphere. Connecting the dry atmosphere with the surface of the liquid is an atmosphere of increasing humidity, completely saturated at all times at the immediate liquid surface.

The rate of evaporation from this surface into a gas is obviously so dependent upon the relative rates of diffusion of the vapor and of the gas, provided the vapor moves away from the liquid surface, at a rate slow enough not to interfere with the establishment of equilibrium conditions between the vapor and liquid phases. The maintenance of an equilibrium condition at the surface, will in turn depend upon the constancy of tem-

¹ See below. A very complete annotated bibliography on evaporation is furnished by *Monthly Weather Review*, Washington, June, 1908, to June, 1909.

² *Mem. lit. phil. soc.*, 5, 536 (1802).

³ *Loc. cit.*

⁴ The evaporation constants calculated on the basis of Dalton's law deviated from the mean by from 1.4 to 4.5% for a given experiment. Values calculated by means of Stefan's law showed corresponding deviations of from 1.2 to 5%.

perature, the length of the moist atmospheric column, and the absence of violent stirring effects in the gas. If we neglect these precautions we are not at all sure that the surface gas layer is saturated with liquid, and what we measure then, is not in reality the relative rates of diffusion of the two gases, but the combined effects of wind and diffusion.¹ This is equivalent to the statement that evaporation proceeds in two steps, the first a simple change of phase, the second a diffusion of vapor away from the liquid surface.

In this research definite working conditions have been established which yield a measure of the relative diffusion rates by an evaporation method. We should, therefore, anticipate that the velocities will be in harmony with Graham's law of inverse square roots of the densities, and that the method itself, like that of Bunsen, will furnish a means of determination of the molecular weights of gases. The following data represent the results obtained in a series of experiments carried out as above described.

TABLE I.

Bottle 1 (6 mm. diam.).				
Gas.	dW/dT (gms./hr.).	dT (hrs.).	B (corr.).	$B \times dW/dT$.
Air.....	0.0008836	74.92	750.0	66.31×10^{-3}
Air.....	8623	135.5	754.7	65.06
Air.....	8743	141.42	753.8	65.89
Air.....	856	192.92	756.5	64.76
Air.....	8700	166.25	754.3	65.63
Air.....	8573	144.17	751.0	64.36
	8673			65.34 Mean
CO ₂	0.0006070	144.83	751.2	45.59
CO ₂	6250	147.0
CO ₂	6505	144.83	750.5	48.87
CO ₂	6255	215.1	756.8	47.39
CO ₂	6100	191.1	752.8	45.99
CO ₂	6023	189.3	750.4	45.17
	620			46.60 Mean
H ₂	0.002947	136.2	749.8	221.2
H ₂	296	119.17	752.6	222.7
H ₂	2858	220.8	750.2	214.6
.....	3044	139.6	756.5	230.4
	2952			222.2 Mean

¹ It should be pointed out that as the experiments were conducted the atmosphere held a fixed position throughout, relative to the liquid surface, and that it was water vapor, not air, which steadily diffused.

TABLE I (continued).

Bottle 2 (1 mm. diam.).

Gas.	$\delta W/\delta T$ (gms./hr.).	δT (hrs.).	B (corr.).	$B \times \delta W/\delta T$.
Air.....	0.0001142	210.1	750.0	8.59×10^{-3}
Air.....	1128	142.1	753.7	8.50
Air.....	1127	166.8	754.2	8.50
Air.....	1134	144.62	751.0	8.52
	1133			8.52 Mean
H ₂	0.0003991	145.75	751.2	30.00×10^{-3}
H ₂	348	430.47	752.0	26.17
H ₂	361	214.7	756.8	27.32
H ₂	359	190.9	752.8	27.03
H ₂	365	189.3	750.3	27.39
	367			27.58 Mean
CO ₂	0.0000679	137.07	752.6	5.11
CO ₂	816	118.93	752.6	6.14
CO ₂	801	221.0	750.5	6.01
CO ₂	829	475.5	754.6	6.26
.....	707	140.0	756.5	5.35
	766			5.77 Mean

Bottle 3 (4 mm. diam.).

Air.....	0.000610	145.8	750.2	45.76×10^{-3}
Air.....	608	147.7	750.5	45.63
Air.....	602	430.8	752.0	45.24
Air.....	593	214.3	756.8	44.85
Air.....	594	191.7	752.8	44.73
Mean.....	602			45.24 Mean
CO ₂	0.000445	190.1	756.5	33.67
CO ₂	427	167.3	754.2	32.17
CO ₂	424	145.3	751.0	31.84
Mean.....	432			32.56 Mean
H ₂	0.002220	136.3	752.6	167.0
H ₂	2158	119.0	752.6	162.5
H ₂	2071	220.67	750.5	156.3
	2052	140.5	759.6	155.2
	2123			160.3 Mean

Calculated on the basis of Graham's law of inverse squares, hydrogen diffuses 3.79 times as fast as air and 4.67 times as fast as carbon dioxide, and air, 1.24 times as fast as carbon dioxide. The results from Table I are as follows:

RELATIVE DIFFUSION RATES.

	H ₂ /Air.	H ₂ /CO ₂ .	Air/CO ₂ .
Bottle 1.....	3.40	4.77	1.40
Bottle 2.....	3.24	4.78	1.48
Bottle 3.....	3.54	4.93	1.39
Mean.....	3.39	4.83	1.42

Further experiments on evaporation are being conducted in this laboratory, and the results of an investigation with a somewhat modified apparatus will be published at an early date.

Applications.—(1) The difference in the rates of evaporation of water into different gases may be used as a method of comparison between the molecular weights of gases. (2) The dependence of rate of evaporation upon the nature of the gas suggests that the feeling of warmth caused by carbon dioxide upon the nerves of the hand¹ may be due to retardation of the normal rate of perspiration. (3) The explanation of higher and more constant terrestrial temperatures in previous geologic eras notably in the carboniferous, may be connected with the slower evaporation of water into an atmosphere rich in carbon dioxide.²

SEATTLE, WASHINGTON.

{CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY.
No. 256.]

THE ELECTRICAL SYNTHESIS OF COLLOIDS.

By H. T. BEANS AND HERBERT E. EASTLACK.

Received September 27, 1915.

I. Previous Work.

Since the discovery by Bredig³ of the electrical dispersion method of preparing metallic hydrosols and its modification by Svedberg⁴ for the preparation of metallic organosols, very little conclusive experimental work has been brought forward with the object of a satisfactory explanation of the phenomenon.

Kutscherow,⁵ from a study of the dispersion of bi-metal alloys in alcohol by Svedberg's method, found the amounts of the two metals in the highly dispersed colloidal condition to be proportional to their equivalent weights, and he concluded that the process was of an electrochemical nature, leading to an atomically dispersed condition, which was followed by condensation to the colloidal condition. The thermo-mechanical process

¹ Goldscheider, *Gesammelte Abhandlungen*, 1, 305 (1898).

² See Arrhenius, "Worlds in the Making."

³ *Z. angew. Chem.*, 11, 951 (1898); *Z. Elektrochem.*, 4, 514 (1898).

⁴ *Ber.*, 38, 3616 (1905); 39, 1703 (1906); also "Herstellung Kolloider Lösung Anorganische Stoffe," 1909, p. 423ff.

⁵ *Z. Chem. Ind. Kolloide*, 11, 165 (1912).

which he assumed to *accompany* electrical colloid synthesis resulted only in the formation of a coarse dispersion which settled out rapidly.

Benedicks¹ criticised Kutscherow's inexact method of distinguishing between, and separating, the highly and the coarsely dispersed portions of the metal and his arbitrary choice of equivalent weights for metals of variable valence. From his own experimental results,² consisting of a careful study of the action of the arc on the electrode surfaces in the formation of "*Schmelzkratern*" and "*Schmelzkugeln*," and a comparison with the effects produced on other surfaces (asphalt, paraffin, etc.) by purely thermo-mechanical means, and also from a consideration of the total heat of fusion, thermal conductivity, and other properties of the metals in relation to their ease of dispersion, he concluded that electrical colloid synthesis was a purely thermo-mechanical process.

Quite recently an article has appeared by Mukhopadhyaya³ in which an attempt has been made to add experimental evidence on the nature of the electrical synthesis of colloids. Although his opinions are in accord with those of Benedicks, there is nothing conclusive in the work.

II. Purpose of the Investigation.

Up to the present time the hypothesis that electrical colloid synthesis consists of a thermo-mechanical dispersion, as pictured by Benedicks and others,⁴ has been sufficient, but, in view of new experimental facts, the former theory now becomes inadequate. The object of the present paper is to show that, in addition to a primary pulverization, the actual synthesis of the colloid is much more dependent upon a secondary process, which is of the nature of a chemical reaction between the metal and certain substances present, or formed in the dispersion medium during the preparation of the colloid. As the authors are of the opinion that this secondary process is of a similar nature to that assumed to be operative in the so-called "complex" theory of colloid formation, it will be necessary to consider some of the work that has been done in connection with the development of that theory.⁵

III. The Complex Theory of Colloids.

The idea that there is an intimate association with hydrosols of certain small amounts of electrolytes, which cannot be removed without impairing the stability of the sol, goes back to the time of Graham. Indeed, it has long been known that, to convert certain hydrogels into hydrosols, peptization by means of electrolytes is necessary.

¹ *Z. Chem. Ind. Kolloide*, 11, 263 (1912).

² *Kolloidchem. Beih.*, 4, 229 (1912).

³ *THIS JOURNAL*, 37, 292 (1915).

⁴ Cf. Freundlich, "*Kapillarchemie*," 1909, p. 311; Von Weimarn, "*Grundzüge der Dispersoid Chemie*," 1911, p. 83.

⁵ For a more complete discussion and references see Cassuto, "*Der Kolloide Zustand der Materie*," 1913, pp. 190-214.

Picton and Linder¹ have long regarded the hydrogen sulfide which they always found associated with metallic sulfide sols, and which could not be removed by indifferent gases, as an essential constituent of the sol.

Jordis and Kanter² showed that a small amount of acid, or alkali, increased the stability of silicic acid sol and the former³ was unable to prepare a stable hydrosol free from electrolyte.

Lottermoser,⁴ in a series of researches on hydrosols of difficultly soluble silver salts, found that a negative silver iodide hydrosol was formed by the addition of a dilute solution of silver nitrate to one of potassium iodide. The sol was stable so long as the potassium iodide was in excess. A positive sol was formed by the addition of the potassium iodide solution to an excess of the silver nitrate. When the solutions were brought together in equivalent amounts, the sol was unstable and precipitation occurred. His theory to explain these facts was that the hydrosols owed their existence to the formation of a complex between the colloid and that ion of the colloid which was present in excess.

Svedberg⁵ found that the critical temperature (the temperature at which coagulation takes place) for electrically prepared platinum sols in commercial ether was higher than in carefully purified material, and was led to investigate the effect of the addition of small amounts of foreign substances to the pure medium. The nature of the curves obtained by plotting the critical temperature against the amount of substance added indicated that a stable sol in an absolutely pure medium would be impossible.

These observations are in accord with those of Duclaux.⁶ He showed, for example, that the precipitate formed by the interaction of potassium ferrocyanide and copper chloride always contained potassium, no matter what excess of copper chloride was used. He considered that chemical complexes were formed and disputed the contention that the presence of the third ion was due to mechanical adsorption or occlusion. He investigated these sols in various stages of dialysis and found that the stability of the sol decreased as the purification continued. He therefore concluded that the stability of the sols depended upon the presence of certain amounts of electrolyte which he designated as the "active part" of the colloid.

Von Weimarn⁷ considers that peptization is an important factor in the stabilization of sols and that it consists in the conversion of a practi-

¹ *J. Chem. Soc.*, 61, 114 (1892); 87, 1906 (1905).

² *Z. anorg. Chem.*, 35, 16 (1903).

³ *Ibid.*, 44, 200 (1905).

⁴ For a summary and earlier references see *Z. phys. Chem.*, 70, 239 (1910).

⁵ *Kolloid Z.*, 2, 142 (1907).

⁶ *J. chim. phys.*, 5, 29 (1907); 7, 405 (1909).

⁷ "Grundzüge der Dispersoid Chemie," 1911, pp. 75-79 and 90.

cally insoluble substance into a compound whose solubility meets the requirements necessary (according to his theory) for the formation of a stable sol. He holds, however, that it is incorrect to assume that a sol cannot be obtained in an absolutely indifferent medium in the absence of a peptizing agent.

In general, therefore, it seems certain that the stability of hydrosols is vitally connected with the presence of small amounts of foreign substances usually related to, or derived from, the colloid itself, and it is upon this basis that the chemical or complex theory of colloids has been developed. The hypothesis, briefly stated, is that the particles of a hydrosol consist essentially of a complex between a substance of very low solubility and an ion of an electrolyte, the presence of which is necessary to the stability of the sol. A sol is stabilized only by certain ions and when these are removed or replaced coagulation occurs. The colloid owes its charge to the ion which stabilizes it.

IV. Are Sols of the Noble Metals Exceptions to the Complex Theory?

The sols of the noble metals, especially when prepared by electrical dispersion in "pure" water, have been considered exceptions to the complex theory.¹

Bredig,² however, has recommended the use of 0.001 *N* alkali (NaOH) instead of pure water in the preparation of gold sols by his method. In referring to this point Whitney and Blake³ state that "a more concentrated and more stable gold solution may be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a conductivity of 200×10^{-6} ."

These two isolated instances of the stabilization of electrically prepared hydrosols by the addition of foreign substances, suggested that perhaps other electrolytes would be found to have a similar effect, and even suggested the possibility that these hydrosols were *not* exceptions to the complex theory of colloids. The fact that stable hydrosols have been prepared by electrical dispersion methods, without the addition of electrolyte, might then be explained either by the assumption that sufficient electrolyte was formed during the process of dispersion, or that the water used already contained the electrolyte necessary for the stabilization of the colloid in accordance with this theory.

In regard to the first of these assumptions, it is well known that when

¹ Cf. Freundlich, *Loc. cit.*, pp. 323-4 and 360; Cassuto, *Loc. cit.*, p. 213; Taylor, "The Chemistry of Colloids," 1915, p. 110.

² "Anorganische Fermente," Dissertation, Leipzig, 1901, p. 26.

³ THIS JOURNAL, 26, 1376 (1904), footnote. This statement was not discovered until after the present work including the preparation of red gold sols in 0.0005 to 0.002 *N* HCl had been completed. The conductivity 200×10^{-6} for hydrochloric acid corresponds to a concentration of about 0.0005 *N*, lying well within this range of concentration.

the more electropositive metals, *e. g.*, copper,¹ cadmium,² iron,³ and lead,⁴ are electrically dispersed in water the sols consist partially or entirely of the metallic hydroxide. McIntosh⁵ observed that the conductivity of electrically prepared silver sol was 40 to 60 times that of the water used (2.2×10^{-6}). Blake⁶ found the freshly prepared silver sol to be alkaline to phenolphthalein, and more recently the work of Kohlschütter⁷ and of Rebière⁸ has shown that a considerable portion (15 to 45%) of the total silver may be present as oxide or hydroxide. Indeed, even in the case of platinum, the work of Graeser⁹ indicates that a certain amount of oxidation takes place when this metal is dispersed in the presence of air.

There are clearly two points open to experimental work which may throw some light on the nature of electrical colloid synthesis and possibly on the theory of colloids in general: (1) the relative extent to which oxidation of the metal (formation of ion) takes place during the preparation of gold and platinum sols, and (2) the nature and generality of the stabilizing effect of certain electrolytes in the preparation of gold sols as observed in the two cases noted above.

V. Oxidation in the Dispersion of Gold and Platinum.

The method employed in studying this point was to measure the increase in conductivity when gold and platinum sols are prepared in very pure water. While it is perfectly certain from the work of Kohlschütter¹⁰ and of Rebière¹⁰ that all of the electrolyte present in the sol does not contribute equally to its conductivity (probably on account of adsorption by the colloid) and quantitative results cannot therefore be expected, a qualitative idea of the relative amounts of electrolyte formed may be obtained from such measurements.

The Conductivity of the Colloid.

That any increase in conductivity is not due to the colloid itself¹¹ may

¹ Paine, *Kolloidchem. Beih.*, 4, 24 (1912).

² Bredig, *Z. physik. Chem.*, 32, 127 (1900).

³ Schmauss, *Physik Z.*, 6, 506 (1905).

⁴ Burton, *Phil. Mag.*, [6] 11, 425 (1906).

⁵ *J. Phys. Chem.*, 6, 15 (1902).

⁶ *Am. J. Sci.*, [4] 16, 431 (1903).

⁷ *Z. Elektrochem.*, 14, 49 (1908).

⁸ *Compt. rend.*, 148, 354 (1909); 154, 1540 (1912).

⁹ *Dissertation*, Leipzig, 1903; cf. Freundlich, *Loc. cit.*, p. 324.

¹⁰ *Loc. cit.*

¹¹ The prevailing confusion in regard to the conductivity of colloids arises more from an indefinite conception as to the constitution of a colloid than from experimental differences. It is generally admitted that the conductivity of a colloid is small compared to that of ordinary electrolytes—yet to just what extent the conductivity of a sol is due to the colloid proper seems to be a matter of considerable doubt. Cf. Stewart, "Recent Advances in Physical and Inorganic Chemistry," 1912, p. 93; Freundlich, *Loc. cit.*, p. 337; Cassuto, *Loc. cit.*, p. 45; and Taylor, *Loc. cit.*, pp. 62-5.

be reasoned from two viewpoints. First, the charge on the colloid is in all probability due to ions associated with it and any effect of removing ions already present in the medium or of decreasing their mobility would be to decrease the conductivity—as would also the adsorption of the molecular portion of the electrolyte. Second, the conductivity due to the colloid proper may readily be calculated from the mobility of the particles in an electric field and their number in a given volume. The necessary data are readily obtained from the literature.

The results of previous measurements of the migration velocities of gold and platinum particles are summarized in Table I.

TABLE I.

Sol.	Mobility.	Method.	Author.
Au W. & B.	43.0×10^{-6} cm./sec.	moving boundary in verticle tube	Whitney and Blake ¹
Pt Bredig	34.0×10^{-6} cm./sec.		Whitney and Blake ¹
Au Bredig	21.6×10^{-6} cm./sec.	moving boundary in U-tube	Burton ²
Au Bredig	33.0×10^{-6} cm./sec.		Burton ²
Pt Bredig	20.3×10^{-6} cm./sec.		Burton ²
Au Bredig	26.0×10^{-6} cm./sec.	microscopic	Rolla ³
Au Zsigmondy	26.0×10^{-6} cm./sec.		Rolla
Pt Bredig	24.0×10^{-6} cm./sec.		Rolla
Au not given	6.7×10^{-6} cm./sec.		Coward ⁴

Whitney and Blake do not claim any greater accuracy than to say that the migration velocities are of the same order of magnitude as those of the ions of neutral inorganic salts of monovalent elements. No refinements or great accuracy were attempted in Coward's work. Rolla's and Burton's values agree fairly well, but those of the former are more consistent among themselves and will be used for the purposes of calculation. As a matter of fact, the order of the results would not be affected by the use of either of the extreme values given above.

Zsigmondy⁷ gives the following linear dimensions for the particles of various colored gold sols:

Color of sol.	Average size in μ .			
Rose.....	6			
Deep red.....	10	15	18	32
Violet-red.....	23	32	35	75
Violet.....	35	95		
Blue-violet.....	54			
Dirty blue.....	30			
Purple-red.....	38			
Blue.....	130			

¹ *Loc. cit.*, p. 1365.

² Calculated from data given.

³ *Phil. Mag.*, [6] 11, 425 (1906).

⁴ *Ibid.*, [6] 12, 472 (1906).

⁵ *Atti accad. Lincei*, [17] 2, 650 (1908).

⁶ *Trans. Faraday Soc.*, 9, 149 (1913).

⁷ "Zur Erkenntnis der Kolloide," 1905, p. 104.

The average radius of colloidal gold particles evidently lies between the limits $3\mu\mu$ and $65\mu\mu$.

From the migration velocities and the radii, the charge on gold particles of various sizes¹ may be calculated with the aid of Stokes' Law, $e = 6\pi\eta rv/X$, where e is the charge, η the viscosity of the medium, r the radius of the particle, and v its velocity under a potential gradient X . Putting η for water at $20^\circ = 0.01$, $v = 26 \times 10^{-5}$ cm./sec. when $X = 1$ volt/cm. the charge e for various values of r is obtained. From the weight of gold contained in a known volume of the sol and the radii of the particles the number per cc. (N) is obtained. From the number of particles per cc., their charge, and mobility, the specific conductivity (k) due to the particles is readily calculated. Table II gives the values of e , N and k calculated for various values of r for a sol containing 100 mg. of gold per liter.

TABLE II.

r (cm.).	e (E. S. U.).	N (per cc.).	k (mhos).
10×10^{-7}	16×10^{-10}	124×10^{10}	1.7×10^{-10}
20×10^{-7}	32×10^{-10}	15×10^{10}	0.4×10^{-10}
30×10^{-7}	48×10^{-10}	5×10^{10}	0.2×10^{-10}
40×10^{-7}	64×10^{-10}	2×10^{10}	0.1×10^{-10}
50×10^{-7}	80×10^{-10}	1×10^{10}	0.07×10^{-10}

The conductivity of platinum sols would be of the same order of magnitude.

It is clear that the conductivity due to the colloid itself is negligible compared to those measured. Any increase in the conductivity must therefore be due to the introduction of electrolyte into the sol from one or more of several sources: (1) oxidation of the electrode, (2) impurities present in the electrode materials, (3) combination of foreign substances dissolved in the water, e. g., nitrogen and oxygen, and (4) accidental introduction from outside sources during the preparation. Since the first of these is of primary importance in the present investigation, the others were eliminated, as far as possible, by the use of very pure materials, and the exercise of extreme care in the preparation of the colloid to avoid the accidental introduction of foreign substances.

Materials and Apparatus.

The water used in all the work presented in this paper was freshly distilled from alkaline permanganate, using a block tin condenser, and was collected hot in thoroughly steamed "non-sol" bottles. Its specific conductivity at 25° varied from 0.6 to 1.2×10^{-6} mhos.

The gold and platinum wire used was the purest obtainable from a

¹ According to the theories of Lamb (*Brit. Assn. Report*, 1887, 502) and Smoluchowski (*Bull. Acad. Sci. de Cracovie*, 1903, 182) the rate of migration should be independent of the size and shape of the particles. The experiments of Whitney and Blake, as well as those of Burton, support this view.

reliable firm. The electrodes were made by soldering about 5 cm. of the gold or platinum wire (No. 14, B. & S.) onto copper wires of the same diameter, using silver solder. The electrodes were carefully cleaned, polished with filter paper, and finally rinsed with conductivity water before each experiment. Only the gold or platinum portions of the electrodes came in contact with the water during the preparation of the colloid.

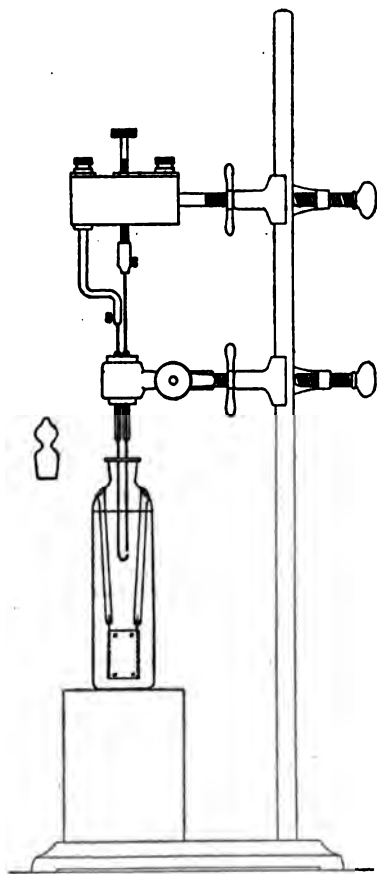


Fig. 1.— $\frac{1}{4}$ actual size.

A conductivity cell and electrode adjustment were so designed (Fig. 1) that the colloid could be prepared in the cell itself and thus avoid the necessity of pouring the sol from one vessel to another. The cell was patterned after the Freas type and had a capacity of about 60 cc. The electrodes were concentric platinum cylinders 13 and 15 mm. in diameter and 25 mm. in height. They were fixed at a distance of about 1 mm. apart by three glass pinions near the top and three near the bottom. The surfaces were sandblasted, but not platinized. The constant of the cell (0.0092) was determined by comparison with a cell whose constant (0.3002) had been accurately determined against known solutions of both sodium and potassium chlorides. No great accuracy was attempted in the determination of the former constant, as all measurements were to be relative. In spite of the extremely low value of this constant, heating effects with solutions of conductivity approaching that of water were negligible. A Leeds and Northrup bridge with a wire about 7

meters in length and connections for reversing the ends was used. The resistances were checked among themselves, but an absolute standardization was unnecessary. All conductivity measurements were made in a thermostat at a temperature of $25^{\circ} \pm 0.01^{\circ}$.

The current for the preparation of the colloid was obtained from the 120 volt, D. C., lighting circuit. In addition to a variable resistance, an inductance coil was made by winding several layers of No. 22 (B. & S.) asbestos-covered wire around an iron pipe 2 cm. in diameter and 75 cm. in length. The coil was surrounded by an iron jacket and was employed

as a principal resistance.¹ It allowed a current of about 5 amperes to pass from the 120 volt circuit and because of its large self induction a good arc could be obtained with a current of 3 to 4 amperes—the strength used throughout this work.

Results of Conductivity Measurements.

A number of experiments were carried out to determine the relative increase in conductivity in the preparation of gold and platinum sols. The arcing was continued for about one minute in each case, or until sols of approximately the same depth of color were obtained. Of a number of results those given in Table III are typical.

TABLE III.

Gold.			Platinum.		
$k_{H_2O} \times 10^6$	$k_{sol} \times 10^6$	$\Delta k \times 10^6$	$k_{H_2O} \times 10^6$	$k_{sol} \times 10^6$	$\Delta k \times 10^6$
1.03	1.62	0.59	0.89	4.28	3.39
1.10	1.14	0.04	0.73	3.49	2.76
0.99	1.14	0.15	0.78	3.81	3.03
0.96	1.24	0.28	0.88	4.11	3.23
1.12	1.62	0.50			
0.94	1.55	0.59			
0.58	0.75	0.17			
0.90	1.67	0.77			
0.83	1.18	0.35			
Average $\Delta k = 0.4 \times 10^{-6}$ mhos.			Average $\Delta k = 3.1 \times 10^{-6}$ mhos.		

The average increase in conductivity is seen to be nearly 8 times greater for platinum than for gold. Since equal precautions were taken in the preparation of the two sols, the difference must for the most part be due to a greater oxidation in the case of the platinum. The important observation was made that *the platinum sols were invariably more stable than the gold*. All the gold sols were blue or bluish purple and usually precipitated in from 2 to 24 hours. The platinum sols on the other hand remained apparently unchanged on standing several weeks.

Thus, earlier evidence in regard to the relationship between the stability of these sols and the presence of small amounts of certain electrolytes is confirmed. The question as to the amount and nature of the electrolyte necessary for this stabilization still remains.

VI. The Stabilization of Gold Sols by the Addition of Electrolytes.

The average increase in conductivity in the preparation of the platinum sols was found to be 3.1×10^{-6} mhos, which would correspond to the presence of 0.0001 to 0.0003 *N* concentration of free electrolyte, depending upon the mobilities of the ions. The concentrations of alkali and hydrochloric acid, mentioned above in connection with the stabilization

¹ We are indebted to Professor Thos. B. Freas for assistance in the designing and construction of this coil.

of gold sols, are much greater than this, but, as will be seen from the following experiments, the addition of these, as well as of certain other electrolytes in concentrations of this order, to the water in which gold is dispersed effects a very marked stabilization of the sol.

In order to study the effect of electrolytes in the preparation of gold hydrosols, these sols were formed by striking an arc between pure gold electrodes immersed in solutions of the substances under investigation. The apparatus for this procedure was the same as that previously described, except that the conductivity cell was replaced by a thoroughly steamed flask of about 40 cc. capacity. The salts used were recrystallized from conductivity water and then either dried at 115° or fused in a platinum dish. From the salts, thus purified, stock solutions of 0.01 *N* concentration were made by weighing out the salt and making up to definite volume at 25° , using conductivity water. The solutions of lower concentration were made by diluting the stock solutions with conductivity water.

The results of these experiments are given in Tables IV–XII. The uniform manner in which the color of the sol varied from one concentration of electrolyte to another, made confirmation of the results by duplication of the experiments unnecessary. In some cases this confirmation was made, but the results are not given. The variation in color was so gradual that no sharp definition of the limiting values of the concentrations of electrolyte in which red, stable sols were obtained, could be made. The ease and certainty with which the results could be duplicated, however, is illustrated by the data given in Table XIII.

TABLE IV.—SODIUM HYDROXIDE.

Conc. NaOH.	Color of sol.	Remarks.
0.00005 <i>N</i>	purple	} unchanged in 18 hrs.
0.0001	purple	
0.0002	tinge of blue	
to	red,	}
0.0005	decreasing amount of blue	
0.0007		
0.001		} pure red after 18 hrs.
0.002	} pure red	
0.003		
0.004		
0.005		
0.01	reddish purple	} deep bluish purple after 18 hrs.
0.02	bluish purple	
0.03	blue	

pptd. in 18 hrs.

pptd. in 2 hrs.

TABLE V.—HYDROGEN CHLORIDE.

Conc. HCl.	Color of sol.	Remarks.
0.00005 <i>N</i>	pure red	all pract. the same color remaining unchanged for weeks sharp change between 0.002 and 0.003 <i>N</i>
0.0001		
0.0003		
0.0005		
0.0007		
0.001		
0.002	bluish purple	precipitated in 3 days precipitated in 2 days
0.003		
0.004		

TABLE VI.—SODIUM CHLORIDE.

Conc. NaCl.	Color of sol.	Remarks.
0.0001 <i>N</i>	reddish purple	The red sols were united, evaporated on a water bath to a 0.002 <i>N</i> conc. of NaCl, filtered, and set aside for two months, at the end of which time the sol was apparently unchanged
0.0002	pure red	
to		
0.004	tinge of blue	
0.005		
to	red,	
0.009	increasing amount of blue	
0.01	bluish purple	

TABLE VII.—AMMONIUM CHLORIDE.

Conc. NH ₄ Cl.	Color of sol.	Remarks.
0.00005 <i>N</i>	red, faint tinge of blue	} pure red after 2 days
0.0001	} pure red	
to		
0.002		
0.003	red, trace of blue	} reddish purple after 2 days precipitated in 2 days
0.005	purple	

TABLE VIII.—POTASSIUM CHLORIDE.

Conc. KCl.	Color of sol.	Remarks.
0.00001 <i>N</i>	purple	The color was little changed in any of these sols after stand- ing 24 hrs.
0.00002	reddish purple	
0.00005	faint tinge of blue	
to	red,	
0.0002	decreasing amount of blue	
0.0003	pure red	
to		
0.003		
0.004	red, faint tinge of blue	
0.005	red, with more blue	
0.0075	purple	
0.01	purple	

TABLE IX.—POTASSIUM BROMIDE.

Conc. KBr.	Color of sol.	Remarks.
0.0001 <i>N</i>	purple	None of these sols had precipitated appreciably after standing 4 days
to		
0.0004	tinge of blue	
0.0005	pure red	
to		
0.001	red, tinge of blue with increasing of blue, to deep purple	
0.002		
to		
0.005		

TABLE X.—POTASSIUM IODIDE.

Conc. KI.	Color of sol.	Remarks.
0.0001 <i>N</i> to 0.0007	violet-purple with increasing amount of red	On standing overnight all of these sols had changed to about the same color—reddish violet to transmitted light and a golden red to reflected light. (See remarks below on these sols)
0.001 to 0.003	red, tinge of blue	
0.004 to 0.006	tinge of blue red, purple	

TABLE XI.—BARIUM CHLORIDE.

Conc. BaCl ₂ .	Color of sol.	Remarks.
0.00002 <i>N</i>	reddish purple, decreasing amount of blue	practically unchanged after 2 days
to		
0.00004	pure red	
0.00005		
to	partially pptd. in 2 days completely pptd. in 1 day completely pptd. in 3 hrs. completely pptd. in 3 hrs.	
0.0001		
0.00015		red, tinge of blue
0.0002		reddish purple
0.0003		bluish purple
0.0005		blue, trace of red
0.0007		blue
0.001		blue

TABLE XII.—SODIUM CARBONATE.¹

Conc. Na ₂ CO ₃ .	Color of sol.	Remarks.
0.0001 <i>N</i>	bluish purple	} After 3 days the blue tinge had entirely disappeared.
0.0002	reddish purple	
0.0003	red, tinge of blue	
0.0005	} red, all with faint tinge of blue	
to		
0.003		
0.005	reddish purple	
0.01	purple	

¹ Extrapolation from the curve obtained by plotting $\log V_m$ (molar volume) against $\log \alpha$ (percentage of hydrolysis) indicates that at concentrations below 0.0007

Potassium fluoride,¹ nitrate, sulfate, chlorate, and sulfuric acid were tried in the same manner over similar ranges of concentration. Without exception the sols obtained were dirty blue in color and coagulated completely on standing for a few hours.

It is seen that hydroxide, chloride, bromide, and iodide ions, when present within certain limits of concentration in the water in which gold is electrically dispersed, exert a marked stabilizing action on the sol formed. The effect is *not* obtained by dispersion in pure water and subsequent addition of the electrolyte.

The upper limit of concentration seems to depend somewhat on the precipitating power of the cation present. Thus the upper limit for barium chloride, where the bivalent cation has a high precipitating power, is much less than for the chlorides of sodium, potassium, and ammonium. The relation does not seem to hold among the latter ions themselves and other factors undoubtedly aid in the determination of the upper limit of concentration.

The lower limit of concentration is seen to correspond closely in several cases with the concentration of electrolyte produced in the preparation of platinum sols in pure water. The amount of electrolyte formed in the latter case is then sufficient to account for the fact that the stability of that sol is greater than that of gold sol in pure water. It was thought possible that the lower limit of concentration might depend upon the amount of colloid formed, *i. e.*, with smaller amounts of colloid formed, red sols might be obtained in lower concentrations of electrolyte. Sols were therefore next prepared by arcing the gold for different periods of time in the same concentration of electrolyte. The sols were then diluted in Nessler tubes until the same density of color was obtained and the colors compared.

TABLE XIII.

0.00001 <i>N</i> KCl.		0.0001 <i>N</i> KCl.	
Time of arcing.	Color of sol.	Time of arcing.	Color of sol.
5, 10, 15, 20 and 25 sec.	purple	10, 20, 30, 45 and 60 sec.	red, tinge of blue

No difference in the colors of the sols of either series was apparent and there seems to be no relation between the color and the concentration of the colloid near the lower limit of electrolyte concentration.

Fluoride, nitrate, sulfate, and chlorate ions do not stabilize the gold sols. In fact, the sols prepared in solutions containing these ions are *N* sodium carbonate would be completely hydrolyzed (cf. Morgan, "Elements of Physical Chemistry," 1914, p. 367). The above red sols in sodium carbonate solutions can be attributed to the concentration of hydroxide ion present rather than to any specific action of the carbonate ion.

¹ The C. P. salt was recrystallized from conductivity water in platinum vessels and fused in a platinum dish. The 0.01 *N* solution was practically neutral to litmus, although more concentrated solutions were preceptibly alkaline.

much less stable than those prepared in conductivity water. It is to be noted that these ions do not form stable compounds with gold, while chloride, bromide, iodide, and hydroxide, mentioned above as stabilizing the sols, form its most stable compounds. This point is of especial interest in the exceptional behavior of fluorine as compared with the action of the other halogens. From its great chemical activity it would be expected that gold fluoride would be among the most stable compounds of gold, yet fluorine appears to have little, if any, affinity for this metal. Lenher¹ has shown that "gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions." That this unusual behavior should be duplicated in the behavior of fluoride ion toward gold hydrosol points strongly to *a relation between the stabilizing effect and the ability of the ion to form a stable compound with gold*. This indication is born out by the behavior of the other ions which do not readily form stable compounds with gold and likewise do not stabilize the hydrosol.

Compounds, if formed, should be present to the greatest extent in the red chloride sols. An examination of the filtrates obtained after coagulation of several of these sols with hydrochloric acid was made to determine the presence of any soluble gold compounds. So far all results have been negative. Apparently the amount of gold compound necessary to stabilize the sol is either extremely minute or is so firmly attached to the colloidal particles that it is not removed from the coagulum by washing with hydrochloric acid.

The red sols obtained in chloride, bromide, and hydroxide solutions are very similar in color and stability. The iodide sols, however, are quite different in color and much less stable. This suggests that an examination of the absorption spectra and a quantitative investigation of the stability of the other sols would show differences there also. Work along these lines is being undertaken. The iodide sols present an appearance which suggests the presence of free iodine. Treatment with carbon disulfide or starch fails, however, to show any trace of the free element.

On standing, any of these sols gradually deposits gold in the form of a fine, yellow powder which, upon examination under the microscope, appears to be made up of spherical particles ranging in diameter from 5μ down and very similar to the "*schmelzkugeln*" described and photographed by Benedicks. The rate at which the gold settles out decreases as the sol stands, as shown by the fact that a sol in 0.0001 *N* hydrochloric acid, which contained 100 mg. of gold per liter when first prepared, analyzed 84 and 73 mg. per liter after standing 10 and 50 days, respectively.

It was of interest, especially in the case of the hydrochloric acid sols,

¹ THIS JOURNAL, 25, 1136 (1903).

on account of the reversal of the charge on many negative colloids by hydrogen ion,¹ to examine the direction of migration of the particles in an electric field. A cell for the observation of electrophoresis was designed, which, on account of its ease of construction and manipulation, warrants description. A 25×75 mm. object glass, 2 mm. in thickness, was ground to the form shown in Fig. 2 and cemented to a similar unground

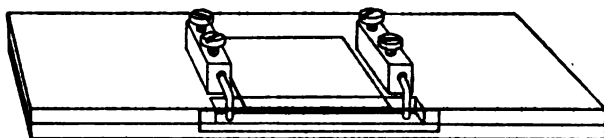


Fig. 2.—Actual size.

glass. A narrow strip cut from a cover glass closed the front of the trough. Binding posts for the platinum electrodes were cemented into place as shown. A potential of from 4 to 6 volts with the electrodes about 2 cm. apart gave a sufficiently rapid motion to the particles to be readily observed. The advantage of this type of cell over those previously described² is that it combines ease of cleaning and filling with the use of small amount of the liquid. The volume is, however, sufficient to avoid the interference of the "reverse movement" near the walls³ with the observations. Disturbing effects due to liberation of gases at the electrodes are also small.

The cell was set up on the stage of a Siedentopf-Zsigmondy ultramicroscope and gold sols in sodium, potassium, and hydrogen chlorides, sodium hydroxide, and potassium iodide were examined. In each case the colloid migrated toward the anode and is therefore negatively charged. The hydrogen ion does not, therefore, have the effect of reversing the direction of migration of the gold particles in these sols.

VII. Conclusions Concerning the Nature of the Electrical Synthesis of Colloids.

From a consideration of the experimental evidence brought out in this investigation it seems that electrical colloid synthesis must be considered as being essentially more than a thermo-mechanical dispersion. It may be pictured as taking place in two distinct steps, the second of which is dependent upon the conditions produced by the first:

(1) a thermo-mechanical action by which the metal is dispersed in a molten or vaporized state as supported by the experiments of Benedicks, and

¹ Cf. Perrin, *J. chim. phys.*, 2, 601 (1904).

² Cotton and Mouton, *Ibid.*, 4, 365 (1906); Ellis, *Z. physik. Chem.*, 78, 321 (1911); and Coward, *Loc. cit.*

³ Cotton and Mouton, *Loc. cit.*

(2) the formation of a colloidal complex between the highly dispersed metal, at a high temperature produced by the arc, and certain ions present in the medium.

The data are too meager to enable one to decide definitely as to the nature of this complex, the formation of which takes place simultaneously with the condensation of the dispersed metal in the liquid or vaporized state to the solid. It might be conceived to depend upon the action of certain ions as condensation centers, similar to the condensation of super-saturated water vapor upon dust particles or ions in a gas. The condensation of water vapor might be supposed to take place more readily on dust particles of calcium chloride than on particles of a chemically indifferent substance. By analogy, since a greater chemical potential exists between the atoms or ions of chlorine and of gold, for example, than between those of fluorine and gold, the former would very probably furnish points of condensation more readily than the latter. The initial stage of such a condensation would be chemical reaction in the ordinary sense. Subsequent growth of the particles would depend upon certain physical conditions, *e. g.*, increased radiation with the growth of the particle tending to increase its ability to serve as a point of condensation. In a pure medium, or one which contains no stabilizing ion, the dispersion takes place, but, owing to the lack of condensation centers, the condensation occurs at fewer points and the particles are consequently larger. The dispersion then behaves as an ordinary suspension and settles out rapidly. This would account for the great instability of gold sols in conductivity water and of Svedberg's metal organosols in pure media. The increased stability of the sols obtained in the presence of stabilizing ions is not alone, however, to be considered as dependent upon the increased dispersion obtained. The presence of these ions in the particles of the colloid constitutes in itself a stabilizing factor. It does not seem likely that the whole of the particle consists of a single chemical substance, and there can be little doubt that these sols, as well as those of metallic sols in general, regardless of their method of preparation, consist of essentially more than a dispersion of metallic particles in an indifferent medium.

VIII. Summary.

It has been shown that:

1. The specific conductivity due to the colloid proper of metallic hydrosols of average concentrations is, by calculation from reliable data, of an order of 10^{-10} mhos or about 0.0001 of that of conductivity water.
2. The oxidation of metal, *i. e.*, the formation of ion, which takes place during the electrical dispersion of platinum in water is considerably greater than in the case of gold.
3. Electrically prepared platinum sols in water of conductivity less than 1.2×10^{-6} mhos are much more stable than similar gold sols.

4. The free electrolyte formed in the above platinum sols (as distinguished from that which may be adsorbed and takes relatively little part in the conductivity) corresponds to an electrolyte concentration of 0.0001 to 0.0003 *N*.

5. The presence of chloride, bromide, iodide, or hydroxide ion in concentrations ranging from 0.00005 to 0.005 *N* (approximately) has a marked stabilizing effect on gold sols, and furnishes a quick and reliable method of preparing these sols.

6. The stabilizing effect is not produced by dispersion of the gold in pure water and subsequent addition of the electrolyte.

7. The upper limit of electrolyte concentration for a particular anion seems to be governed somewhat by the precipitating power of the cation.

8. The lower limit of electrolyte concentration required to produce a red sol is, within a wide range, independent of the concentration of colloid formed.

9. The particles in all of these red sols have been shown by electrophoresis to be negatively charged.

10. The stabilizing effect is not observed on the addition of fluoride, nitrate, sulfate, or chlorate ion in similar concentrations.

11. The stabilizing effect seems to be closely related to the ability of the ion to form stable compounds with gold. No gold, however, could be detected in the filtrate obtained after coagulation of the sol. The amount of gold compound necessary to stabilize the colloid is probably extremely minute.

12. Electrical synthesis of colloids is considered to consist of a thermo-mechanical dispersion of the metal which is followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

In conclusion we desire to express our appreciation of generous assistance and advice from members of this department and of the Department of Physics.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY FOR GAS INVESTIGATIONS, U. S. BUREAU OF MINES.]

THE CRITICAL CONSTANTS OF NORMAL BUTANE, ISO-BUTANE AND PROPYLENE AND THEIR VAPOR PRESSURES AT TEMPERATURES BETWEEN 0° C. AND 120° C.

By F. M. SHERBURN and G. A. BURRELL.¹

Received September 27, 1915.

In this report, one of a series dealing with the vapor pressures of gases, are shown the critical constants of *N*-butane, isobutane and propylene

¹ Published by permission of the Director of the Bureau of Mines.

and their vapor pressures at temperatures from 0°C. up to 120°C. These data had not been previously determined. They were needed by this laboratory in work on the liquefaction of gases at different temperatures.

Preparation of Gases.

The physical properties of substances in the neighborhood of their critical points are seriously affected by the presence of minute traces of impurities; hence it is of the utmost importance to obtain as pure material to work with as possible. Therefore, extreme care was exercised in the preparation of the gases selected for the work. Final purification was accomplished in every case by fractionating the gases at low temperatures. In some cases, for instance in separating normal butane, normal boiling point -0.3° , from possible traces of isobutane, normal boiling point¹ -13.4° , fractionation was conducted at a pressure of less than 1 mm. of mercury; hence the process was tedious to carry out by working with a hand-operated vacuum pump, and, therefore, the operation was made automatic, as described later.

Isobutane.—Isobutane was prepared by the reaction between isobutyl iodide and the zinc-copper couple. The evolved gas was collected over caustic potash. Next it was introduced into a bulb surrounded by liquid air, and atmospheric air or other gases of sufficient vapor pressure at the temperature of liquid air were removed by repeated fractionations with a Töpler pump. Fractionation of the gas was repeated until no more gas was given off. Next the gas was fractionated at a temperature of -120° to -115° . At this temperature the vapor pressure of normal butane is practically nil (it is 1 mm. at -99.9°) and the vapor pressure of isobutane is below 1 mm.² This procedure freed the isobutane of any possible traces of normal butane. Fractionating at -120° to -115° was tedious, hence the operation was made automatic by connecting a bulb immersed in liquid air with the bulb containing the liquid gas under examination. As a result the gas distilled over into the liquid-air bulb with but little attention from the operator. After about three-fourths of the liquefied gas had distilled the distillation bulb was sealed off. This process was repeated about 10 times, the whole operation requiring one week's time. Of course, water vapor and other gases whose vapor pressures are entirely negligible at a temperature of -120° to -115° are also removed at the same time. But as further precaution the gas was fractionated several times at a temperature of about -98° . At this temperature the vapor pressure of isobutane is about 7 mm., hence fractionation proceeded faster.

Normal Butane.—This was prepared by the reaction between normal

¹ Lebeau, *Chem. Zentr.*, 1908, II, 292, gives -10.5° and Noyes, *THIS JOURNAL*, 34, 142 (1908) gives -11.5° .

² See *THIS JOURNAL*, 37, 2188 to 2193, 2482 to 2486 (1915).

butyl iodide and the zinc-copper couple. It was collected over caustic potash and purified by fractionation at low temperatures.

Propylene.—Propylene was prepared by dehydrating propyl alcohol with phosphoric anhydride. It was collected over caustic potash and purified by fractionation at low temperatures.

Criteria of Purity.

1. The vapor pressures determined by the authors were independent of the relative volumes of liquid and vapor.
2. The logarithm of the pressure plotted against the reciprocal of the absolute temperature gave a straight line.
3. The critical phenomena were normal and different samples of condensed liquid gave identical results both as to vapor pressure and critical constants.
4. All the vapor in the experimental tube could be condensed to the liquid phase without a perceptible rise of pressure.

The Critical Constants.

Critical Temperature.—Young¹ defines the critical temperature as the temperature at which the volume of saturated vapor and that of the liquid are equal.

When a gas is compressed below its critical temperature the volume of the liquid increases, the vapor decreases and a sharp meniscus is present. As the critical point is approached the meniscus becomes flatter and less distinct; finally a mist or opalescence appears within a small range of temperature. It should make no difference from which side the critical temperature is approached: the same phenomena at the same temperature should be reproduced from either side. The critical point was taken to be that at which no meniscus was visible when the volume was constant, and at which it just appeared when the volume was slightly increased. In the duplicate experiments of the authors the critical temperatures never differed by more than 0.1° .

Critical Pressure.—The critical pressures were determined by means of the compression machine shown in Fig. 1² and read by means of the air manometer when the critical temperature was reached.

Calibration of Manometers.—The air manometers (e) and (d), Fig. 1, consisted of two capillary tubes with white backgrounds, having an internal diameter of about 0.8 mm. and a length of about 500 mm. They were graduated in millimeters and accurately calibrated by filling them with mercury and allowing any desired portion to flow through a small capillary stopcock sealed to the tubes. The volumes were calculated

¹ *Proc. Roy. Dublin Soc.*, 12, 407 (1910).

² Similar in most respects to one used by Sidney Young and constructed at this laboratory by O. P. Hood, chief mechanical engineer and W. F. Hausstein, instrument maker, and F. E. Donath, glassblower.

from the weights of mercury drawn off. After the tubes had been calibrated over their entire length, one end of each was closed and the volume up to a chosen mark which had not been affected by the sealing-off process was obtained by introducing mercury through a very fine hair-like tube,

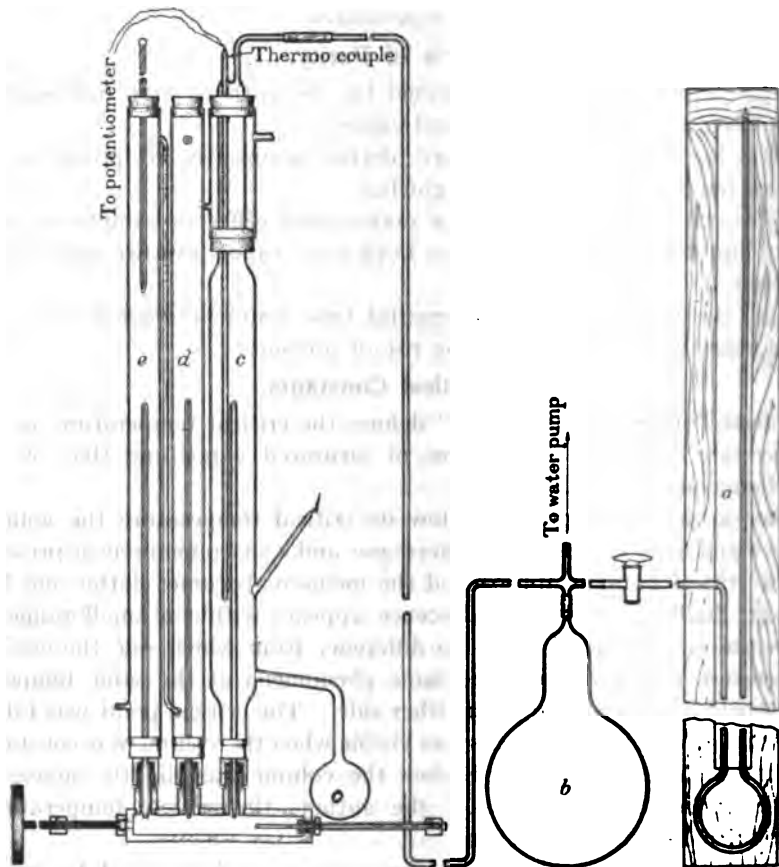


Fig. 1.—Compression apparatus for determining critical data and vapor pressure.

noting the position of the mercury in the tube and then withdrawing it with the same small tube and weighing it. After several check operations the volume of the closed end, with reference to a graduation on the tube, was determined by weighing the mercury drawn off.

One of the tubes served as a high-pressure and the other as a low-pressure manometer. The low-pressure tube was then blown out slightly at the open end so that a small ridge was formed which prevented it from slipping from its rubber cap when introduced into the compression machine.

To the high-pressure tube (*e*), Fig. 1, a small bulb was sealed, so that a much larger mass of air could be introduced. The capacity of this

bulb was about 3 cc. In filling these manometers with air both tubes were sealed to a common train which was in turn sealed to a Töpler pump containing a large tube of phosphoric anhydride. After the tubes had been thoroughly exhausted, dry and CO_2 -free air was introduced into them. They were then evacuated, filled with air, again evacuated, etc., nine or ten times, and finally filled at about atmospheric pressure with air which had been passed over phosphoric anhydride and soda lime several hundred times. The ends were then sealed off and scratched with a file so that they could be broken off beneath the mercury in the pump. Next they were fitted into their rubber caps, their ends broken in the reservoir of the compression machine and screwed tightly into the machine.

PV was obtained for the low manometer by fitting into the third opening in the compression machine a long capillary tube, of about 2-mm. diameter, open at both ends, and observing the difference of levels of mercury in the open tube and the low manometer corresponding to several different positions of the mercury in the manometer.

TABLE I.
Barometer = 741 mm.

Low manom. reading. Division number.	Vol. of air at 0° C.	Temp. manometers. ° Aba.	Temp. of open manom. Room temp. ° C.	Diff. of levels corr. to 0°.	Pressure mm. Hg. at 0°.	PV z.
340.0	0.2373	297.7	27.0	107	898	213.1
320.0	0.2365	297.7	27.0	161	902	213.3
300.0	0.2217	297.7	27.0	220	961	213.0
280.0	0.2069	297.7	27.0	289	1030	213.1
260.0	0.1920	297.7	27.0	369	1110	213.1
240.0	0.1774	297.7	27.0	460	1201	213.05
220.0	0.1624	297.7	27.0	569	1310	212.7
201.0	0.1482	297.7	27.0	693	1434	212.5

Mean value of PV = 213.0.

TABLE II.

High-gage reading. Division number.	Vol. of air at 0° C.	Low-gage reading.	Vol. of air at 0°.	Diff. of levels.	Pressure from low gage reading.	PV.	Pressures recalc. from av. PV.
340.0	0.2094	125.5	0.0919	221	2539	531.6	2536
300.0	0.1838	108.0	0.0792	199	2888	530.8	2890
320.0	0.1964	116.9	0.08547	210	2702	530.6	2704
260.0	0.15825	91.9	0.06704	175	3352	530.6	3356
240.0	0.1447	84.0	0.0606	160	3674	531.6	3671
220.0	0.1332	76.5	0.05547	150	3989	531.3	3987
200.0	0.1206	69.1	0.0499	138	4406	531.4	4404
180.0	0.1082	61.9	0.0445	125	4911	531.4	4909
140.0	0.0836	47.9	0.0341	100	6346	530.1	6354
120.0	0.0713	41.0	0.0289	87	7455	531.5	7450
100.0	0.05928	34.5	0.02402	75	8942	530.1	8957
70.0	0.04144	24.7	0.01663	54	12862	533.0	12818

Mean value of PV = 531.2.

Table I gives the data employed in calculating PV for the low-pressure manometer used in this work.

The foregoing set of observations was used to obtain PV for the high-pressure manometer, as follows:

The open tube was removed from the compression machine and a small plug of glass inserted in its place in the cap. The plunger was screwed up until the mercury in the high-pressure gage appeared on the graduations. Readings were then taken on both gages.

The data obtained for the high gage are given in Table II.

The figures in the sixth column of Table II were calculated from

$$P = \left(\frac{\text{PV (for low gage)}}{\text{Observed volume} \times 273/T} + \text{difference of levels in gages} \right).$$

Method of Filling the Tubes with Substances for Investigation.—The tubes (c), Fig. 1, to contain the condensed gases were about 500 mm. long and had an internal diameter of about 2.5 mm. One end was sealed up and on the other end a small ridge was blown to prevent it from slipping from the rubber cap in the compression machine. This latter end was then drawn out very thin (in order to facilitate subsequent sealing off) and sealed to a train to which a bulb was also sealed. Pure gas introduced beforehand into a Töpler pump was then condensed in the bulb by means of liquid air and pumping carried on until all traces of air (possibly accidentally introduced) were removed from the gas. Several evaporations and condensations were always made and the pumping continued to be sure that no air was present. Finally some gas was condensed in the experimental tube and then allowed to evaporate. About 1 to 1½ inches of liquid gas was then condensed with liquid air in the tube and all the excess gas pumped off. The tube was then sealed off, scratched with a file, and set in the compression machine. By this method of sealing, alteration of the gas by the flame of the blowpipe did not occur, because at the temperature of liquid air the vapor pressures of the gases are negligible and hence no vapor was present at the point of sealing. Next the piston of the compression machine was driven up until the tip of the tube was broken off beneath the mercury, whereupon the latter rushed into the tube and trapped the liquid gas.

Method of Carrying Out a Determination.—After the tube (c) Fig. 1, containing the gas, was screwed tightly in the compression machine, the jacket shown in Fig. 1 was set and some lead oxide mixed with glycerol applied to the stopper supporting the jacket in order to make a tight joint.

Some mercury was poured down the side tube (h, Fig. 1) to cover the rubber stopper and the substance (in one experiment chlorobenzene boiling under different pressures) which served for maintaining the desired jacket temperature was introduced into the bulb o, through the same

side tube, (*h*, Fig. 1). It was then closed with a plug of glass and a rubber tube. The liquid in the bulb was then boiled by means of a gas flame and the pressure on the vapor therein read by means of a scale (*a*, Fig. 1), and regulated by means of a water pump. The temperature was approximately read from tables given by Travers.¹

The final temperature readings were obtained by means of a potentiometer and a copper-constantan thermocouple calibrated² against a mercury thermometer in turn calibrated by the Bureau of Standards. Temperatures were read to 0.02°. The arrangement is shown in Fig. 1.

When the vapor in the jacket tube was at the required temperature, readings of the vapor pressure were taken with the liquid and vapor occupying different volumes. The best procedure, as has been pointed out by Young,³ was to condense all the vapor by increasing the pressure by means of the piston and then draw out the piston again while ebullition took place. Readings were taken with the vapor occupying a small volume and again when it occupied a larger volume.

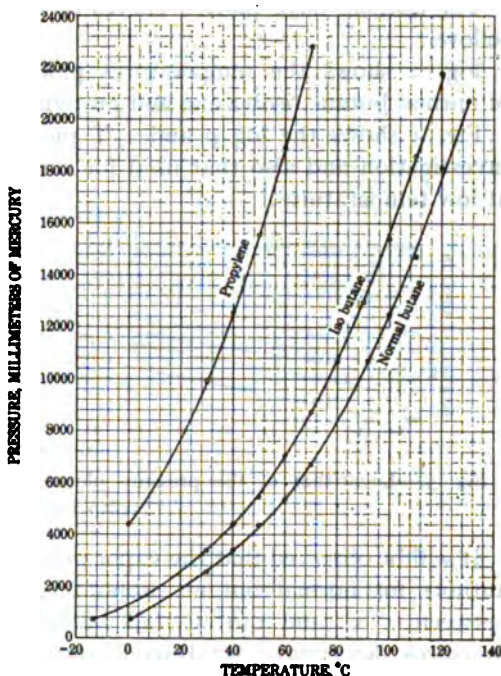


Fig. 2.—Temperature, °C plotted against pressures, mm. of Hg.

TABLE III.

Method of Calculating the Vapor Pressure of Propylene at 50°.

Gage reading.	Temp. of manom. °C.	Vol. of air at 0°.	PV/V at 0°.	Diff. of levels in two tubes.	Amagat's correction.	P.
58.0	24.0	0.03446	15414	+217	—120	15511
58.1	24.0	0.03455	15374	+310	—120	15564

When the vapor and liquid were in equilibrium the machine was tapped with a stout block of wood in order to cause the mercury columns to settle. Next readings were taken from the high-pressure gage. The pressure

¹ "Experimental Study of Gases," 1902, pp. 317, 318.

² Calibrated with the assistance of J. K. Clement, physicist of the Bureau of Mines.

³ *Proc. Roy. Dublin Soc.*, 12, pp. 396 (1910).

was obtained from PV of the high-pressure gage, also from the difference of levels of mercury in the experimental and manometer tubes. A correction was applied for the compressibility of air as determined by Amagat.¹

The authors could check their temperatures within 0.1° and their pressures within 0.5%.

Curves.

The authors have plotted curves of the results of the investigation as follows:

Fig. 2 shows the temperatures plotted against the vapor pressures of normal butane, isobutane and propylene, respectively.

Fig. 3 shows the $\log p$ and $1/T$ plot for the substances used in this investigation and also that used for the measurement of vapor pressures at low temperatures.

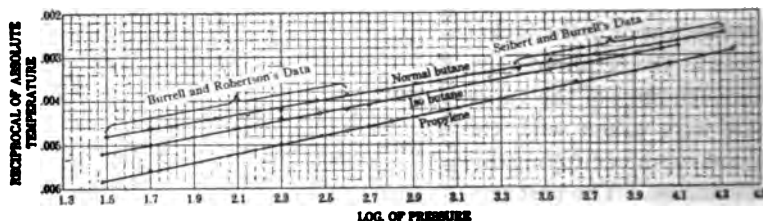


Fig. 3.—Logarithm of the pressure plotted against reciprocal of the absolute temperature.

It will be observed that the vapor pressures as determined by the present authors for normal butane, isobutane, and propylene at temperatures between 0° C. and 130° C. fall on the same straight line as the vapor pressures determined by Burrell and Robertson at low temperatures.¹

In Table IV are shown the critical data for the three gases under investigation, also a and b as calculated from van der Waals' equation.

TABLE IV.—CRITICAL DATA.

Substance.	Temp. 0° C.	Press. Mm. Hg.	Press. Atmos.	a .	b .
Normal butane.....	153.2	27113	35.67	0.02883	0.005470
Isobutane.....	133.7	27771	36.54	0.02562	0.005096
Propylene.....	92.6	34463	45.34	0.01668	0.003692

a and b were calculated from van der Waals' equation:

$$a = \frac{27}{64(273)^2} \frac{T_h^3}{p_h} \quad b = \frac{1}{8.273} \frac{T_h}{p_h}$$

In Table V are shown the vapor pressures of the three gases at different temperatures.

¹ Given in Traver's book on "The Experimental Study of Gases," page 234.

² THIS JOURNAL, 37, 1915, 2188 to 2193, 2482 to 2486 (1915).

TABLE V.

Temp. ° C.	Pressure (mm. Hg.).		
	Iso-butane.	Normal butane.	Propylene.
130	...	20600	...
120	21700	18100	...
110	18600	14700	...
100	15400	12500	...
90	13000	10700	...
80	10650	...	27400
70	8700	6700	22800
60	7000	5400	18900
50	5600	4300	15500
40	4400	3350	12600
30	3400	2550	9900
0	4400

Summary.

The critical data for propylene, normal butane, and iso-butane are given. Vapor pressures of these three gases at temperatures ranging from 0° C. to 130° C. are also shown.

The authors are indebted to Dr. G. A. Hulett, consulting chemist, and to I. W. Robertson, junior chemist to the Bureau of Mines, for valuable assistance in conducting this work.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE LABORATORY FOR GAS RESEARCH OF THE U. S. BUREAU OF MINES.]

THE VAPOR PRESSURES OF SULFUR DIOXIDE AND NITROUS OXIDE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.

By G. A. BURRELL AND I. W. ROBERTSON.

Received September 29, 1915.

In this paper, one of a series, dealing with the vapor pressures of substances at low temperatures, are shown the vapor pressures of sulfur dioxide and nitrous oxide. The method of procedure has been described in previous communications to THIS JOURNAL.¹

Preparation of Gases.

Sulfur Dioxide.—This was prepared by the action of sulfuric acid on copper. It was bubbled through water to remove sulfur trioxide and finally thoroughly fractionated at the temperature of liquid air to remove atmospheric air or other gases of high vapor pressure at that temperature, and at temperatures between —70° and —100° to remove water vapor and other gases of negligible pressures at those temperatures. Purification was carried to the point where the entire liquid boiled within a range of 0.2°.

Nitrous Oxide (N₂O).—Nitrous oxide was prepared by heating ammo-

¹ THIS JOURNAL, 37, 1893, 1902, 2188, 2193, 2482, 2486 (1915).

nium nitrate. The evolved gases were passed through caustic-potash solution and sulfuric acid and finally thoroughly purified by fractionation at low temperatures. In the vapor-pressure observations, readings were made with a rising and falling mercury column, and checked after boiling away a part of the *liquid gas* in the vapor-pressure bulb.

In Tables I and II are shown the observed and calculated vapor pressures for the two substances, the temperatures given being the average of one reading each on thermometers Nos. 707 and 504. The equations of the curves were calculated from the Nernst formula¹

$$\log p = \frac{\lambda}{4.571T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C.$$

In the case of sulfur dioxide the constants λ , ϵ , and C were found by taking the values of p at the temperatures 262.1°, 248.3° and 208.6° Abs. In the case of nitrous oxide the values of p at 182.5°, 173.6°, and 152.0° Abs. were taken. Above 182.5° Abs. nitrous oxide is liquid and below this temperature it is solid. In this case only the solid phase was considered in calculating pressures.

TABLE I.
Saturated Vapor Pressures of Sulfur Dioxide at Low Temperatures.

Temperature. Average.		Pressure.	
0° C.	Abs.	Obs. Mm. Hg.	Calc. Mm. Hg.
Liquid			
—11.0	262.1	760	760
—11.9	261.2	730	735
—13.0	260.1	700	697
—14.7	258.4	650	647
—16.4	256.7	600	599
—20.3	252.8	500	499
—24.8	248.3	400	400
—30.4	242.7	300	292
—37.8	235.3	200	196
—42.3	230.8	150	149
—48.3	224.8	100	101
—57.5	215.6	50	52
—64.5	208.6	30	30
Solid			
—72.9	200.2	16	15
—76.0	197.1	12	11
—81.3	191.8	7	6
—87.4	185.7	3	3
—94.4	178.7	0.5	0.2

Equation of curve = $\log P =$

$$-1951.46/T + 1.75 \log T$$

$$-0.01277T + 9.4408$$

¹ "Theoretical Chemistry," 1911, p. 719.

TABLE II.
Saturated Vapor Pressures of Nitrous Oxide at Low Temperatures.

Temperature. Average.		Pressure.	
0° C.	Abs.	Obs. Mm. Hg.	Calc. Mm. Hg.
Liquid			
— 88.7	184.4	760	...
— 89.3	183.8	730	...
— 90.1	183.0	700	...
Solid			
— 90.6	182.5	666	666
— 91.0	182.1	650	646
— 91.9	181.2	600	600
— 93.9	179.2	500	500
— 96.4	176.7	400	399
— 99.5	173.6	300	300
—103.7	169.4	200	200
—106.7	166.4	150	149
—110.8	162.3	100	97
—117.2	155.9	50	48
—121.1	152.0	30	30
—127.0	146.1	15	14.3
—131.3	141.8	7	8.0
—138.9	134.2	4	4.2
—144.1	129.0	1	1.2

Equation of curve = $\log P =$

$$-1096.72/T + 1.75 \log T$$

$$+ 0.0005T + 4.8665$$

In Figs. 1 and 2 are shown the plot of the temperature, ° C. and ° Abs. against the pressure, mm. of Hg, and the logarithm of the pressure against

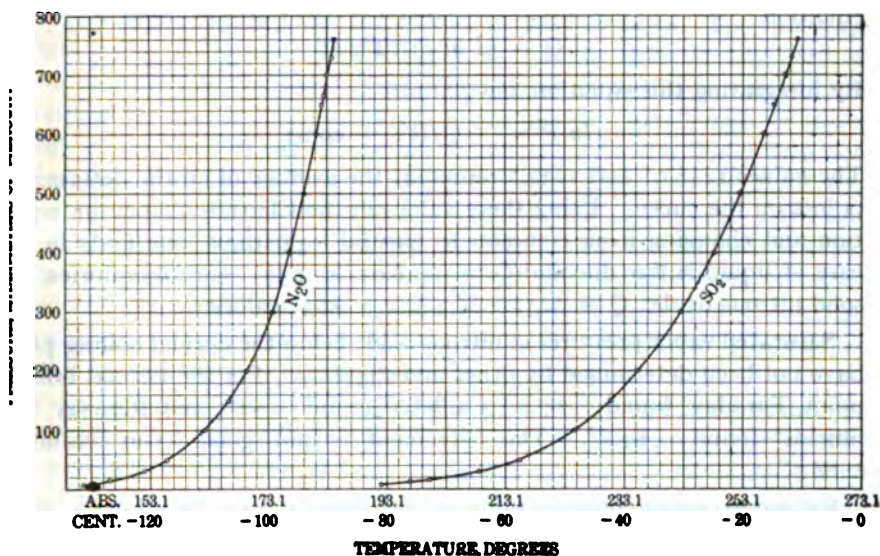


Fig. 1.—Plot of temperature against pressure.

the reciprocal of the absolute temperature. The straight lines shown were drawn by obtaining an equation from the average of all the results

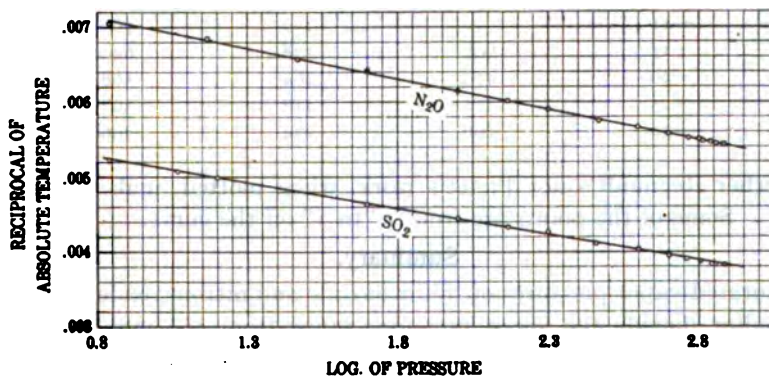


Fig. 2.—Plot of reciprocal of absolute temperature against log. of pressure.

computed by the method of least squares and drawing the lines according to these equations. For liquid sulfur dioxide the equation is

$$\text{Log } P = -1448.01/T + 8.425.$$

For solid nitrous oxide

$$\text{Log } P = -1232.2/T + 9.579.$$

The average heats of evaporation over the temperature range studied (calories per gram-molecules) were calculated from the Clausius-Clapeyron equation

$$Q = (d \ln p)RT^2/dT.$$

By integrating this equation, one obtains

$$\ln P = -Q/RT + \text{const.}$$

The values 1448.01 and 1232.2 represent the average of all the determined points on the curve. Using these values in the Clausius-Clapeyron equation and changing from common to natural logarithms, one finds in the case of liquid sulfur dioxide: $Q = 1448.01 \times 4.571 = 6619$ calories; for solid nitrous oxide: $Q = 1232.2 \times 4.571 = 5632$ calories.

Saturated vapor pressures of nitrous oxide below the normal boiling point have not been determined by other investigators. For the normal boiling point, Faraday¹ found -87.2° , Cailletet² found -92° , and Ramsay and Shields³ found -89.8° . The agreement is not good. Our value is -88.7° .

Saturated vapor pressures for sulfur dioxide have been determined by Regnault⁴ from -30° to 65° , and by Pictet⁵ from -30° to 50° . A comparison of their work with that of the authors of this paper follows:

Temperature. °C.	Pressures (mm. Hg.).		
	Regnault.	Pictet.	Burrell and Robertson.
-10	760	760	...
-11	760
-15	608	578	640
-20	479	464	508
-25	372	418	398
-30	296	274	306

Neither Regnault's nor Pictet's work, when plotted, makes a smooth curve. Some of the points are from 1° to 3° off the curve.

Summary.

Saturated vapor pressures of sulfur dioxide and nitrous oxide are shown. For sulfur dioxide the vapor pressures range from 760 mm. at -11.0° to 0.5 mm. at -94.4° . For nitrous oxide the vapor pressures range from 760 mm. at -88.7° to 1 mm. at -144.1° .

PITTSBURGH, PA.

¹ *Phil. Trans.*, 135, 1, 155 (1845).

² *Arch. de Gen.*, 66, 16 (1878).

³ *J. Chem. Soc.*, 63, 833 (1893).

⁴ *Mem. de l'Acad.*, 26, 535 (1862).

⁵ *Arch. de Genève*, 13, 212 (1885).

NOTE.

An Improved Form of Gas-Washing Bottle.—The ordinary forms of the gas-washing bottle have the following disadvantages: The pressure on the gas is always considerable and is not the same in any part of the apparatus. It not only varies from bottle to bottle but also in the individual bubbles as they rise through the liquid. The length of time during which the bubbles of gas are in contact with the liquid does not depend upon the rate of flow of the gas, but only upon the height of the liquid in the bottle, thus making a large overhead pressure necessary to secure efficient washing. Finally, the liquid is not satisfactorily stirred.

The various forms of apparatus proposed to overcome some or all of these objections are usually not entirely satisfactory, and inevitably complicated in structure and difficult to make. The form proposed is similar in principle to that suggested by Cumming.¹

In its simplest form the apparatus consists of an ordinary bottle, or preferably a square medicine bottle, fitted up as a common wash-bottle, which is laid on its side and has a small side tube at C (as shown in Fig. 1). The gas enters the wash-bottle at F and forms bubbles at the bend,

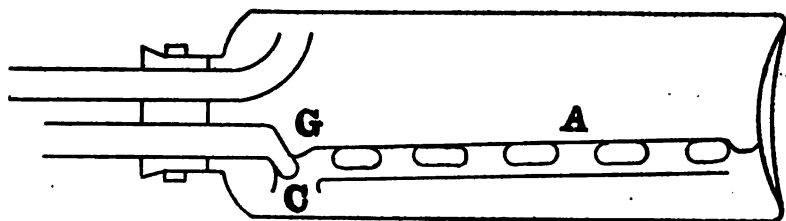


Fig. 1

G in the tube A. The tube A should be of such a size (approximately 5 mm., inside diameter) that the bubbles formed sweep the liquid through it into the bottle, thus causing efficient circulation of the liquid through C. C should be about twice the diameter of the tube A.

The rate of flow of gas in the tube can be varied within considerable limits, and can be made as slow as desired. The character of the washing can be varied by slightly tipping the tube A, or varying the height of the liquid in the bottle. Because of the slow rate at which the bubbles pass through the tube A, the washing is very efficient, and because of the slight head the pressure on the gas can be kept constant, and the amount of spray formed negligible.

These advantages make the bottle described satisfactory not only for ordinary gas washing, but also for saturating a gas with a liquid as in vapor-pressure work. In case the cork is an undesirable feature of the

¹ *Trans. Faraday Soc.*, 6, 10 (1910).

bottle, as is the case in careful vapor-pressure work, or where the cork is subject to attack by the liquid used, the form of the apparatus illustrated in Fig. 2 can be used.

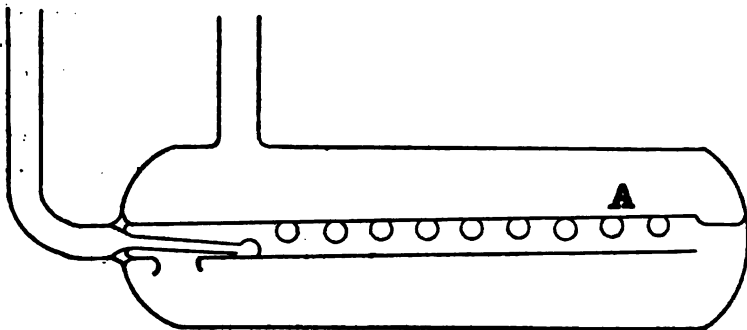


Fig. 2.

The nozzle shown at B, which should have a diameter of about 2 mm., makes the bubbling more regular and the circulation more certain, thus making the latter form preferable to that illustrated in Fig. 1.

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ERRATA.

On p. 2258, October number, line 7 from bottom, for "p. 2238," read p. 2254.

On p. 2261, October number, line 25 from top, for "(p. 2233)" read "(p. 2249)."

On p. 2264, October number, line 21 from top, for "(p. 2244)" read "(p. 2260)."

On p. 2286, October number, footnote 1, for "p. 2268," read "p. 2284."

On p. 2287, October number, footnote 1, for "p. 2274," read "p. 2290."

On p. 2288, October number, footnote 2, for "p. 2273," read "p. 2289."

On p. 2290, October number, footnote 1, for "p. 2270," read "p. 2286."

On p. 2304, October number, footnote 1, for "p. 2286," read "p. 2302."

CORRECTION.

Some of the values given for atomic volumes on page 1646 (37, July, 1915) were taken, in the preliminary draft of the table, from Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. I, p. 854 (1891). It has been intended to substitute later more accurate values, calculated from the more recently found densities and atomic weights of the elements in question, but through an oversight this was not done in every case. The cor-

rected values for the atomic volumes, which should take the place of the old values taken from Ostwald, are as follows: Magnesium, 14.0; silicon, 11.7; white phosphorus, 17.0; calcium, 26.2; chromium, 7.4; iron, 7.5; zinc, 9.2; arsenic, 13.1; bromine, 25.7; molybdenum, 9.4; palladium, 8.7.

Furthermore, the value for the density of arsenic should be given as 5.73, and the true density of aluminum is probably nearer to 2.7 than 2.6, although the latter was Mallet's value.

I am indebted to Professor W. D. Harkins and Dr. R. E. Hall for the discovery of some of these errors.

Fortunately, none of the changes is large enough to effect essentially the curve given on page 1649, or in any way to invalidate the conclusions of the paper in question. Indeed, almost every one of these changes rather improves the agreement of the observed values and those calculated from the equation on page 1652. THEODORE W. RICHARDS.

CAMBRIDGE, MASS., Nov. 4, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

EQUILIBRIA IN THE SYSTEMS OF THE HIGHER ALCOHOLS, WATER AND SALTS.

BY G. B. FRANKFORTER AND STERLING TEMPLE.

Received September 16, 1915.

The dehydration of alcohols is such a common process that it has been studied by many chemists.¹ Foote and Sholes² have studied the general theory of the drying action of a salt on a liquid and the importance of the amount of water which can be taken up by the salt. Frankforter and Frary³ discovered the efficiency of KF as a salting-out agent for ethyl alcohol, worked out a means of testing the strength of alcoholic liquors by means of the action of KF and investigated the equilibria of the following systems: Potassium fluoride-water-ethyl alcohol; potassium fluoride-water-normal propyl alcohol; potassium carbonate-water-methyl alcohol; potassium carbonate-water-ethyl alcohol; potassium carbonate-water-normal propyl alcohol and sodium chloride-water-normal propyl alcohol. It was thought advisable to continue the work of Frankforter and Frary with some of the other alcohols and with some other salts.

¹ Soubeiran, *Ann.*, 30, 356 (1839); Mendeléef, *Z. Chem.*, 1865, 260; Erlenmeyer, *Ann.*, 160, 249 (1871); Smith, *Chem. News*, 30, 235 (1874); Lescoeur, *Bull. soc. chim.*, [3] 17, 18 (1897); Yvon, *Compt. rend.*, 125, 1181 (1897); Ostermeyer, *Pharm. Zeit.*, 43, 99 (—); *Z. anal. Chem.*, 39, 46 (1900); Vitali, *Boll. chim. farm.*, 37, 257 (—); *Z. anal. Chem.*, 39, 46 (1900); *Bull. Chem. Zeit.*, 24, 814, 845 (1900); Young, *J. Chem. Soc.*, 81, 707 (1902); Evans and Fetsch, *THIS JOURNAL*, 26, 1158 (1904); Winkler, *Ber.*, 38, 3612 (1905); Kailan, *Monatsh.*, 28, 927 (1907); Frankforter and Frary, *J. Phys. Chem.*, 17, 402-473 (1913).

² *THIS JOURNAL*, 33, 1309 (1911).

³ *J. Phys. Chem.*, 17, 402-473 (1913).

It has been shown,¹ the salting out of an alcohol belongs to the class of equilibria in ternary mixtures where two liquid phases are possible. Each component, mixed with either of the others, gives a system of only one liquid phase, that of a solution of one in the other. Only when all three components are present can two liquid phases exist. In representing such systems, use is generally made of the system of coördinates founded on the equilateral triangle, either with unit altitude or with the side of unit length.² In the first case, use is made of the fact that the sum of the lengths of the three perpendiculars drawn from a point within the triangle to the three sides is equal to the altitude. The three components of the system are represented by the three vertices, A, B and C; the sides opposite these vertices are lettered *a*, *b* and *c*. Any point O within the triangle represents a mixture of A, B and C in the proportions of and numerically equal to the lines O*a*, O*b* and O*c*, these lines being drawn perpendicular to the sides. In the second case, where the length of a side is taken as unity, the case is the same except that the lines drawn to the sides meet those sides at an angle of 120°. That is, they are drawn to any side in a direction parallel to either of the other two sides.

Some use has also been made of a right-angle isosceles triangle in representing equilibria in ternary mixtures,³ but this is not at all general. In this paper the triangle with sides of unit length will be employed except where rectangular coördinates are used.

Schreinemakers⁴ and others have discussed the general theory of such systems and the application to them of the coördinates based on the equilateral triangle.

Fig. 1 is a general form of the diagram for a ternary system of this class. The three vertices represent the three pure compounds involved;

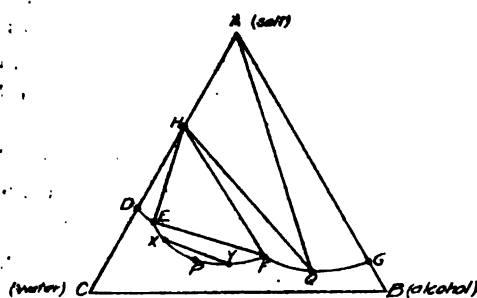


Fig. 1.

any point within the triangle represents a mixture of all three, while any point on a side represents a mixture of the two components represented by the vertices including that side. In Fig. 1 H represents the composition of a solid hydrate of the salt A. D represents the composition of the saturated solution of the salt in pure water, while G represents the

¹ Schreinemakers, *Z. phys. Chem.*, 22, 93, 515 (1897); 23, 649 (1897); Frankforter and Frary, *Loc. cit.*

² G. G. Stokes, *Proc. Roy. Soc.*, 49, 174 (1891); Gibbs, *Trans. Conn. Acad.*, 1896, 3176; Roozeboom, *Z. physik. Chem.*, 15, 147 (1894).

³ Roozeboom, *Ibid.*, 12, 369 (1893).

⁴ Schreinemakers, *Loc. cit.*; Frankforter and Frary, *Loc. cit.*

composition of the saturated solution of the salt in pure alcohol. The line $DEPFQG$ is the locus of all homogeneous mixtures which would be separated into two phases by the addition of an infinitesimal quantity of the salt.

This line $DEPFQG$, which is the boundary between the homogeneous and heterogeneous systems, may be fairly regular throughout its length, but there are three portions which call for separate consideration. The point E represents the solution which is obtained by adding alcohol to a saturated solution of the salt in water until no more alcohol is taken up. This absorption of alcohol by a solution of a salt in water is usually accompanied by a precipitation of some of the dissolved salt. In case the salt forms a hydrate at the temperature used, the point E represents the lower layer of a system of two liquid phases which is in equilibrium with the solid hydrate. The portion DE of the line $DEPFQG$ is thus the locus of all solutions which are saturated with respect to the salt, which contain alcohol in amounts varying from none to the amount in the solution at E and which are in equilibrium with the solid hydrate.

The point F represents the upper layer, *i. e.*, the alcoholic solution of salt and water which is in equilibrium both with the solution at E and with the solid hydrate if one exists, otherwise with the anhydrous salt. Whenever we have the condition of two liquid phases, the lower layer has a composition represented by x , and the upper layer that represented by y . With increasing salt content x approaches the point E , while y approaches F . With decreasing salt content x and y approach the limiting position P and with less than this amount of salt the solution becomes homogeneous. The line EPF is the locus of all values of x and y and is called the binodal curve, the point P is called the plait point and the straight lines connecting x and y are called tie lines. The tie lines may be parallel but are not so necessarily.

The line FQG is the boundary between homogeneous solutions with alcoholic content higher than F and heterogeneous mixtures of such solutions with either the hydrate or the anhydrous salt. The point Q is the limiting value of four areas and by an infinitesimal change in composition may become any one of the following: a homogeneous system below FQG , a mixture of the anhydrous salt with the solution QG , a mixture of the solid hydrate and the solution FQ or a mixture of solution Q with both the anhydrate and the anhydrous salt.

The area $CDEPFQGB$ is the locus of all homogeneous systems. The remaining areas are all heterogeneous and contain either a solid phase or two liquid phases. Area HDE is a mixture of the solid hydrate in equilibrium with a solution represented by some portion of DE . Area EPF consists of two liquid phases only. Area HFQ contains the solid hydrate in equilibrium with the solution FQ . Area HEF contains

centage of water, we obtain Fig. 4, which tells us that the heterogeneous mixture of the three components which contains the maximum amount of water contains neither more nor less than about 22% K F. If we plot the percentage of K F against the percentage of alcohol we obtain Fig. 5, which shows that the K F and the alcohol are able to replace each other to some extent in the solution and that the influence of the K F in producing saturation in a homogeneous system is greater than that of the alcohol for equal weights.

For analytical purposes, the best method of representing the binodal curve in ternary systems of this class seems to be that chosen by Frankforter and Frary, which consists in plotting all alcohol water mixtures on the vertical axis and the number of grams salt per hundred grams solvent on the horizontal axis. In this

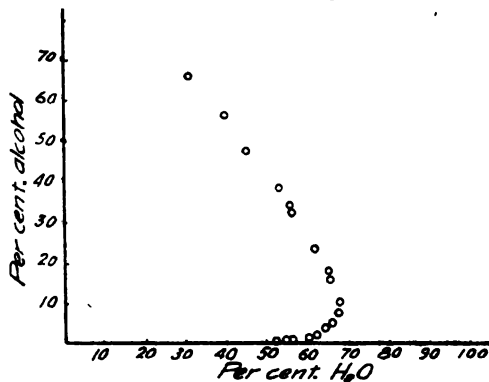


Fig. 3.

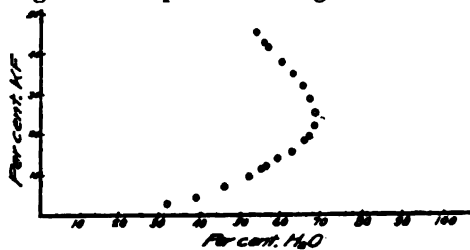


Fig. 4.

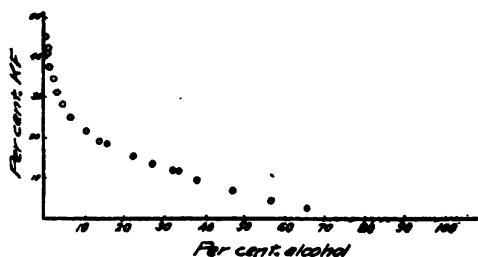


Fig. 5.

method the first set of values are obtained by dividing the weight of alcohol by the combined weight of the alcohol and water and the second set are obtained by dividing the weight of salt by the combined weight of water and alcohol. Thus the solubility of the salt in alcohol of all strengths is shown at a glance and when the solubility of the salt in any alcohol water mixture is known, the strength of the alcohol is read off at once from the curve. Fig. 6 shows this system of plotting, using the same values as those used in Figs. 3, 4 and 5.

Experimental Methods.

An Erlenmeyer flask with a tightly fitting ground glass stopper and a side tube carrying a short thermometer, so placed that the bulb of the thermometer was just above the center of the bottom of the flask, was

used throughout the work. The flask was cleaned, dried and weighed. The salt to be used was transferred directly from the desiccator to this flask, using a wide funnel to prevent any of the salt from adhering to the

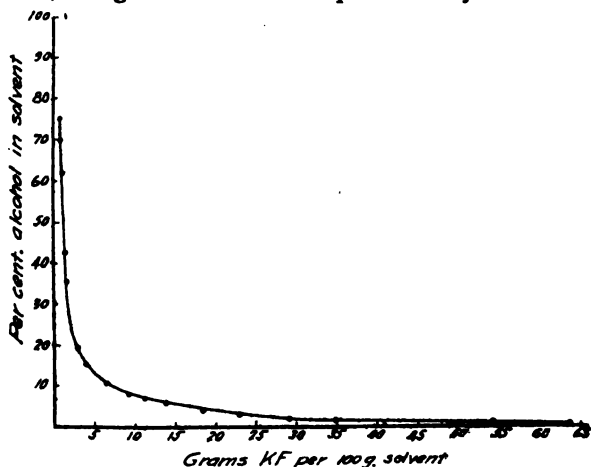


Fig. 2.

neck or sides of the flask. The flask was again weighed, the weight of the salt being obtained by difference. Water was then added from a buret in amount sufficient to just dissolve the salt and the flask and contents were weighed. Alcohol in sufficient quantity to cause a separation into two layers was then added and another

weighing made. Water was now added one drop at a time until the mixture just became homogeneous. After this was weighed all the data for the calculation of the first point on the binodal curve had been obtained.

Successive points on the curve were obtained by adding to this solution, first enough alcohol to cause the appearance of two layers or of a distinct turbidity after shaking and then just enough water to again clear the solution. The flask was kept stoppered, except for the moment when one of the components was being added, and as neither the alcohol nor the water were allowed to come in contact with the neck or upper portion of the inside of the flask, the loss from evaporation was very small.

As the end point was always obtained by adding water from a buret, it is probable that the accuracy in individual tests was frequently not greater than 100 mg. However, these errors, instead of being cumulative, tended to neutralize each other, since after every addition the true amount of water present was determined by weighing the flask and its contents.

All weighings were made on a large Troemner balance, which was easily sensitive to 0.2 mg. under a load of 200 g., but most of the weighings were made to milligrams only. The room in which the work was done was easily kept within 0.5° of 20° during the progress of all the measurements. The temperature of the solution itself at the time of the disappearance of the two layers was never allowed to differ by more than 0.2°

from 20°. As the heat of dilution of the concentrated solutions always tended to produce a rise in temperature on the addition of water, only a little water was added at a time, preventing even a temporary rise of more than 2.0°, and the mixture was always cooled to 20.0° before the final addition of water for clearing the solution, by gentle shaking in an adjoining room where the temperature was kept at about 18°.

As losses by evaporation would cause cumulative errors in case the solvent did not vaporize in the proportions present, several series of determinations were made starting with different points along the binodal curve. For example, the first series might be made by starting with a saturated solution of the salt in water as has been described. The first points in this series would be taken fairly close together, but the later ones farther apart by making successive addition of water and alcohol larger in proportion to the total weight of the contents of the flask as the solution became more dilute. The second series might be begun by making a solution containing only 60% of the amount of salt required for a saturated solution and a third series might start with 40% of the amount of salt needed for saturation. This not only tended to eliminate the cumulative effect of evaporation on the middle and right end of the binodal curve, but also did away with the objection that the decreased sensibility of all the measurements made as the solution became more dilute and larger in amount, rendered the determinations less accurate.

In those experiments where potassium fluoride and sodium chloride were used, spirit blue was chosen as an indicator, barely enough being added to give a clear color to the alcoholic layer. With potassium and sodium carbonates phenolphthalein was used, since these salts destroy the color of the spirit blue.

With increasing percentage of alcohol the consequent decrease in concentration of salt caused a continually decreasing difference in density of the two liquid layers. With solutions containing more than 60% of alcohol the separation into two distinct layers often required 20 minutes or more. However, the end point was more easily determined in these solutions by noting the time when the solution just ceased to be turbid after shaking. In the case of some of the mixtures obtained, a single drop of water would clear a solution which was so turbid that the outline of the thermometer bulb in the solution was only faintly seen.

In handling the flask, the hands were never allowed to come in contact with the sides or bottom of the flask. The flask was lifted by the flange at the top of the neck and when not in the balance was always placed on a sheet of filter paper.

The Purification of Propyl Alcohol.—The alcohol used in the following experiments came from C. F. A. Kahlbaum's factory of Berlin. It was obtained especially for the work tabulated below and represents Kahl-

baum's highest purity. Test indicated, however, that it was not pure. Its boiling point was not constant and its specific gravity did not agree with results obtained by others, who had studied it. On examining the literature, a fairly wide range of variation in the physical constants was found. The variation was due, without doubt, to the extreme difficulty in obtaining the alcohol in perfectly pure form as was indicated in the final purification of the samples in hand. The sample, just as it came from the factory, began to boil at 94.5° under 750 mm. pressure, gradually increasing to 97° as the process continued. The specific gravity changed but little, increasing from 0.7954 to 0.8015. That there was water present as one of the impurities there can be but little doubt; that there was some little ethyl or possibly isopropyl alcohol present seems also quite likely. Work was therefore begun for the purpose of removing the above-mentioned impurities and any others which perchance might be present.

The first attempt to purify the alcohol was made by treatment with the dehydrating substance, potassium fluoride. While the process¹ evidently removed some of the impurities, as water, the sample was by no means pure, after such treatment. After this it was boiled for some hours with powdered quicklime under a reflux condenser, and again redistilled. This treatment again removed some of the impurities, as indicated by the more constant boiling point. It began to boil at 96° and gradually increased to 97.2 at 754 mm. Anhydrous copper sulfate was next tried, but without changing either the boiling point or the specific gravity. Magnesium amalgam was then tried. After standing 24 hours in contact with the amalgam, the alcohol was decanted off and again redistilled. Both the boiling point and the specific gravity approached a constant value, although not entirely so. The sample was finally boiled for several hours with sodium amalgam, again decanted off and redistilled over quicklime. The boiling point was practically constant at 97.5° and 753 mm. pressure. As further treatment failed to change the boiling point, the alcohol was regarded as pure. No attempts were made to determine the nature of the impurities present. There seems to have been an appreciable quantity of water and possibly, as already stated, ethyl alcohol.

The physical constants were then taken with the following results:

B. p. $97.3-5^{\circ}$ at 752 mm.

Sp. gr. (20°) mean of three determinations 0.8032.

The refractive index was taken with the latest type of Pulfrich refractometer at 20° using the hydrogen spectrum tube as the source of light. Three different sets of readings gave the following average values: $H\alpha$ 1.39023, $H\beta$ 1.37651, $H\gamma$ 1.36786.

	Brühl.	Landolt and Jahn.	Zander.	Frankforter and Temple.
Sp. gr.....	0.8044 (20°)	0.8074 (19°)	0.8069 (17°)	0.8032 (20°)
B. p.....	97.2	97.0	97.4	97.3-5

¹ THIS JOURNAL, 36, 1103.

The purified alcohol was kept in a double stoppered bottle until it was to be used. All the experiments tabulated below were made with this purified alcohol.

Purification of Isopropyl Alcohol.—The alcohol used in the following experiments came from Kahlbaum's factory of Berlin. It was bought for pure alcohol, although, as in the case of propyl alcohol, this sample was by no means pure. It evidently contained, as was the case with propyl alcohol, some water, and the careful observation of the boiling point indicated that there was some ethyl alcohol present.

The purification was carried out as in the case of propyl alcohol. The original sample began to boil at 79.5° , after which the boiling point slowly rose to 82° , over half passed over, however, below 82° . Repeated distillation failed to yield more than 40% of the original sample with a boiling point of 82° .

The first purification was made by potassium fluoride. The fluoride raised the boiling point but it was nevertheless not constant. The sample was next boiled under a reflux condenser for several hours with powdered quicklime and again redistilled. The boiling point again indicated further purification. Finally, the partially purified sample was treated with sodium amalgam, the alcohol decanted off, dried thoroughly, again treated with powdered quicklime and redistilled. The boiling point rose to 82° and remained practically constant, rising less than one degree during distillation. The sample thus treated was used in the experiments given below.

The physical constants were then taken and compared with those obtained by others. The following tabulation gives the constants as compared with those given by others:

	Brühl.	Zander.	F. and T.
Sp. gr.....	0.7887 (20°)	0.7861 (17°)	0.7881 (20°)
B. P.....	82.3	82.3	82.5
Refractive index (20°). H_{α} 1.37960, H_{β} 1.36550, H_{γ} 1.35584.			

System: Normal Propyl Alcohol-Sodium Carbonate-Water.—This was the only system containing propyl alcohol which was studied as the systems: propyl alcohol-potassium fluoride-water, propyl alcohol-potassium carbonate-water, propyl alcohol-sodium chloride-water had been thoroughly investigated by Frankforter and Frary. For purposes of comparison, data were sought on the behavior of a single salt with four different alcohols and also on the behavior of single alcohols with four different salts. To make certain that the values obtained were strictly comparable with those obtained by Frankforter and Frary, preliminary sets of readings were made with propyl alcohol, using potassium fluoride and potassium carbonate as the dehydrating salts. All of these results

checked well and could be plotted in on the same curves as those obtained by them.

The system: normal propyl alcohol-sodium carbonate-water has a long binodal curve and is an easy one to measure, as the separation into two layers takes place easily and quickly and the end point with phenolphthalein was easily determined even in mixtures where the solvent consisted of 60% or more of alcohol. Eight sets of measurements were made on this system and three individual measurements in addition. These determinations extended over about a week and the extent of the agreement between successive series, as shown by the curve in Fig. 7, indicates that the method used was at least free from any large variable error. All measurements were made as described under Experimental Methods and the results are shown in Table I, Table II, and Fig. 7.

TABLE I.
System: Normal Propyl Alcohol-Sodium Carbonate-Water at 20.0°.

Solvent added.		Total weight present.			Total contents.	Total solvent.
Water.	Alcohol.	Na ₂ CO ₃ .	Water.	Alcohol.		
12.310	1.771	0.891	12.310	1.771	14.972	14.081
4.102	1.482	0.891	16.412	3.253	20.556	19.665
5.135	3.133	0.891	21.547	6.386	28.824	27.933
11.714	7.555	0.284	11.714	7.555	19.553	19.269
2.394	3.527	0.284	14.103	11.082	25.474	25.190
6.818	11.181	0.284	20.926	23.263	44.473	44.189
14.794	0.756	2.354	14.794	0.756	17.904	15.550
15.413	0.756	2.461	15.413	0.756	18.630	16.169

TABLE II.
System: Normal Propyl Alcohol-Sodium Carbonate-Water.
Grams per 100 g. solvent.

Na ₂ CO ₃ .	Water.	Alcohol.	Na ₂ CO ₃ .	Water.	Alcohol.
6.328	87.423	12.577	2.863	78.020	21.980
4.531	83.458	16.542	2.320	72.580	27.420
3.190	77.138	22.862	1.990	68.463	31.537
1.474	60.972	39.208	1.650	63.519	36.481
1.127	56.006	43.994	1.338	59.204	40.796
0.643	47.356	52.644	1.084	55.438	44.562
15.138	95.138	4.862	1.119	57.292	42.708
15.220	95.324	4.676	0.930	53.067	46.933
11.540	93.458	6.542	0.733	49.449	50.551
8.415	90.824	9.176	0.567	46.125	53.875
6.669	88.779	11.221	0.394	42.413	57.587
5.123	86.396	13.604	0.298	40.493	59.507
4.138	84.215	15.785	0.243	38.913	61.087
3.609	82.823	17.177	0.160	36.432	63.568
2.878	78.901	21.099	0.109	24.841	75.159
			15.363	95.528	4.472
			11.696	93.405	6.595
			16.568	96.591	3.409

System: Isopropyl Alcohol-Potassium Fluoride-Water.—Two series of measurements of this system were made, one starting with 23.474% salt and running to 15.119%, the other between 34.134 and 11.020% by weight of K F. As it was quite difficult to get good end points in the titration of solutions of isopropyl alcohol containing over 20% of the alcohol, *i.e.*, with less than 10% of K F, five separate determinations were made by adding to a solution of K F and water just enough of the alcohol to cause the separation into

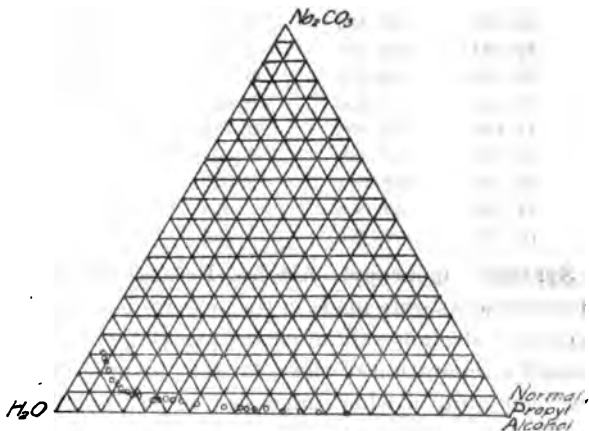


Fig. 7.

two layers, weighing each of the components as it was introduced. The temperature was carefully controlled and kept within $\pm 0.2^\circ$ of 20.0° .

It was expected that the results for isopropyl alcohol would somewhat resemble those obtained by Frankforter and Frary with normal propyl

alcohol, using the same salt. However, on plotting the values obtained, the differences were so great, that it was thought possible that difference in the conditions or in the condition of the salt were responsible and a portion of their work was repeated. As the results all checked with those of the earlier work it

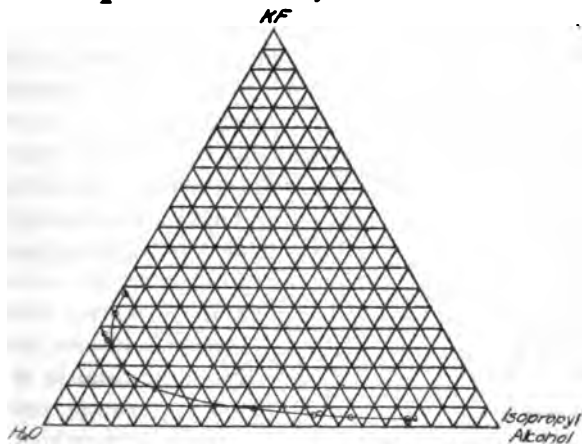


Fig. 8.

was plain that the difference was due to difference in the alcohols alone, and later work, as will be shown, corroborates this view.

The percentage of alcohol present in the solvent ranges from 1.555 to 82.750 and the agreement between the successive values was especially good. The measurements and calculated results are shown in Table III and are plotted in Fig. 8.

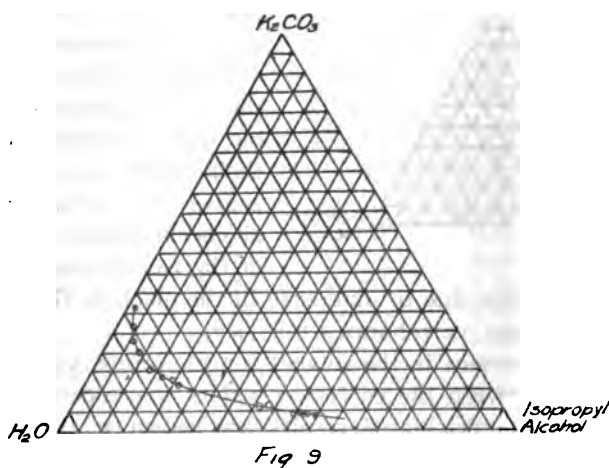
TABLE III.
System: Isopropyl Alcohol-Potassium Fluoride-Water.
Grams per 100 g. solvent.

KF.	Water.	Alcohol.	KF.	Water.	Alcohol.
30.675	97.334	2.666	1.864	19.082	80.918
29.092	95.316	4.684	1.705	17.250	82.750
26.039	93.475	6.525	5.071	40.661	59.339
21.755	91.400	8.600	4.738	52.957	47.043
17.812	87.785	12.215	3.973	34.545	65.455
51.826	98.445	1.555
38.748	97.035	2.965
21.939	91.006	2.994
12.385	78.562	21.438

System: Isopropyl Alcohol-Potassium Carbonate-Water.—A few measurements were made in the systems isopropyl alcohol-NaCl-water and isopropyl alcohol-sodium carbonate-water, but as the addition of alcohol caused a separation of the solid salt, instead of a separation into two layers, over quite a wide range and as end points were very slow, complete curves have not as yet been worked out.

In the system isopropyl alcohol-potassium carbonate-water, four series of measurements were made, the alcohol varying from 2.009 to 55.650% of the mixture and the salt content from 2.869 to 30.979%. The maximum amount of water was found when the solution contained about 19% of salt and 7% of alcohol.

In this system, as in that of isopropyl alcohol-potassium fluoride-water, the values were found to differ greatly from those obtained with normal propyl alcohol and the differences found were entirely similar in the two cases. When plotted in rectangular coördinates the curve for this system more nearly approached a straight line than in any other system of alcohols and water in which potassium carbonate was used.



That is, the isopropyl alcohol and the potassium carbonate were able to replace each other in solutions just in equilibrium in almost constant proportions throughout.

The measurements for this system are shown in Table IV, and the percentages of the three components present are plotted in Fig. 9.

TABLE IV.

System: Isopropyl Alcohol-Potassium Carbonate-Water.

Grams per 100 g. solvent.

K ₂ CO ₃ .	Water.	Alcohol.	K ₂ CO ₃ .	Water.	Alcohol.
13.963	77.633	22.367	17.665	85.605	14.395
13.560	76.901	23.099	15.021	80.555	19.445
13.244	76.081	23.919	3.933	46.735	53.265
44.844	97.089	2.911	3.726	46.188	53.812
36.137	95.217	4.783	3.391	44.797	55.203
28.879	92.651	7.349	2.954	42.706	57.294
24.152	90.841	9.159	6.065	54.603	45.397
..	5.841	53.965	46.035

System: Allyl Alcohol-Potassium Fluoride-Water.—Three sets of measurements were made in this system. The first series was made with a solution containing 2.251 g. of potassium fluoride and the first measurement was made with 7.129% alcohol in the solvent. Alcohol and water were added in succession through ten measurements, bringing the alcohol up to 54.211% of the solvent. A separate determination was made on a solution containing 65.221% of alcohol in the solvent, then a series running from 59.948 to 75.377% alcohol in the solvent and to obtain points at the other end of the curve 10.190 g. of potassium fluoride were dissolved in 20 cc. of water, 0.506 g. of alcohol was added

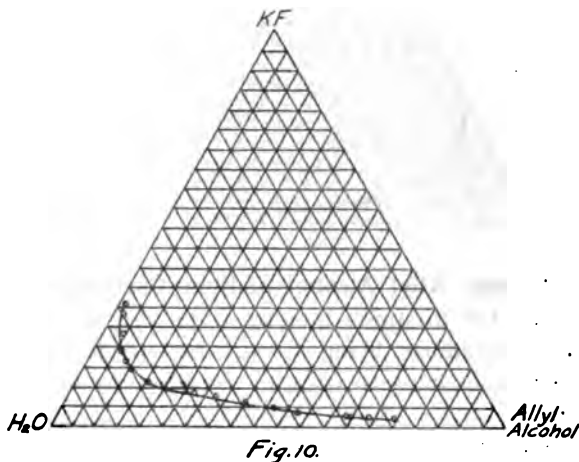


Fig. 10.

TABLE V.

System: Allyl Alcohol-Potassium Fluoride-Water.

Grams per 100 g. solvent.

KF.	Water.	Alcohol.	KF.	Water.	Alcohol.
24.341	92.871	7.129	1.895	34.779	65.221
20.580	90.309	9.691	2.233	36.443	59.948
17.371	88.509	11.491	1.931	34.370	65.630
13.184	82.236	17.764	1.635	31.155	68.845
10.880	77.463	22.537	1.368	28.605	71.395
8.873	70.471	29.529	1.066	24.223	75.377
7.508	64.610	35.390	45.707	97.730	2.270
6.024	57.989	42.011	38.076	96.017	3.983
4.813	52.450	47.550	30.675	94.121	5.879
3.631	45.789	54.211

and water added to just clear the solution which now contained 21.788 g. of water. This solution contained only 2.27% of alcohol in the solvent and two more additions of both alcohol and water were made, bringing the alcohol content up to 3.879% of the solvent.

When plotted in rectangular coördinates the curve for allyl alcohol-potassium fluoride-water closely approaches that of isopropyl alcohol, which it most nearly resembled in slope throughout. The measurements

are recorded in Table V, and the curve is shown in Fig. 10.

System: Allyl Alcohol-Potassium Carbonate-Water.—This system was studied in the same manner as those first mentioned, nineteen readings being taken. The alcohol ranged from 1.424 to 81.159% of the mixture. The results are shown in Table VI and in Fig. 11.

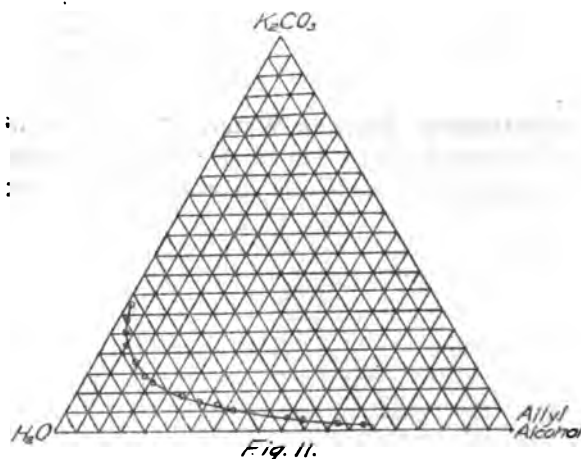


Fig. 11.

System: Allyl Alcohol-Sodium Carbonate-Water.—Values were obtained for mixtures ranging from 16.722% to 60.835% alcohol, only eleven readings being taken. End points at both ends of the binodal curve were hard to obtain. Results are shown in Table VII and in Fig. 12.

System: Allyl Alcohol-Sodium Chloride-Water.—As in the previous system, the end points were rather uncertain with less than 20 or more than 70% of alcohol in the solvent, so record is made only of such readings as seemed most trustworthy, as they suffice to give a very good idea of the general form and slope of the binodal curve.

With allyl alcohol the position of the curves obtained with the differ-

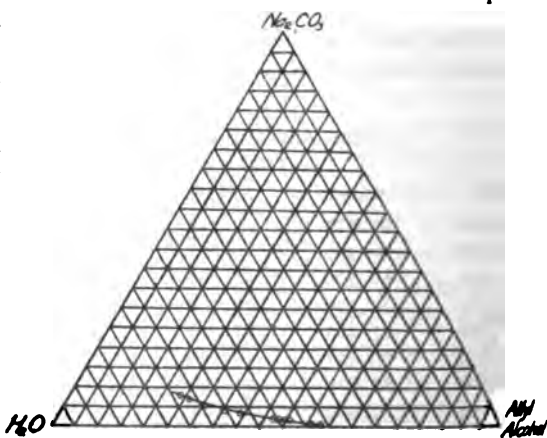


Fig. 12.

ent salts used is much greater than with the propyl or isopropyl alcohol and in consequence any inferences which might be drawn as to the effect of the presence of various ions in the solution should be more evident in the systems containing allyl alcohol as one component.

Results for this system are shown in Table VIII and in Fig. 13.

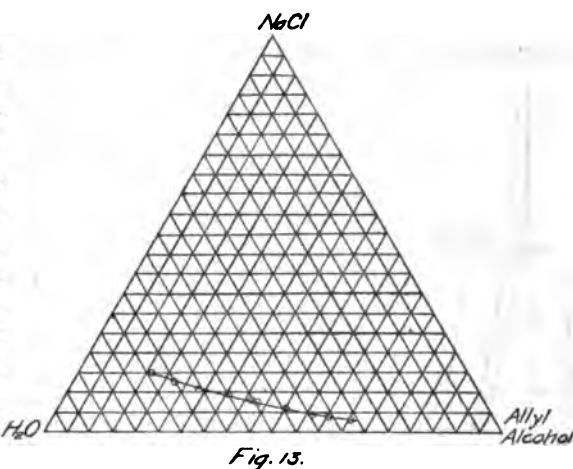


Fig. 13.

TABLE VI.

System: Allyl Alcohol- K_2CO_3 -Water Measured at 20.0°.

Grams per 100 g. solvent.

K_2CO_3 .	Water.	Alcohol.	K_2CO_3 .	Water.	Alcohol.
47.746	97.897	2.103	9.653	73.553	26.447
38.298	96.181	3.819	8.239	69.323	30.677
33.200	94.733	5.267	6.729	64.569	35.431
28.163	93.039	6.961	5.521	60.663	39.337
23.486	90.691	9.309	2.457	48.402	51.598
20.037	88.323	11.677	2.020	45.513	54.487
16.354	84.963	15.037	1.464	41.749	58.251
13.696	81.733	18.267	1.015	37.390	62.610
11.331	77.546	22.454	0.526	31.413	68.587
..	0.0853	18.772	81.228

TABLE VII.

System: Allyl Alcohol-Sodium Carbonate-Water (20°).

Grams per 100 g. solvent.

Na_2CO_3 .	Water.	Alcohol.
10.079	81.593	18.407
7.774	76.247	23.753
6.084	71.584	28.416
4.739	67.834	32.166
3.414	62.874	37.126
2.580	58.948	41.052
1.468	51.891	48.109
1.282	51.026	48.974
1.011	48.070	51.930
0.708	43.666	56.334
0.456	38.888	61.112

TABLE VIII.

Allyl Alcohol-Sodium Chloride-Water (20°).

Grams per 100 g. solvent.

$NaCl$.	Water.	Alcohol.
5.079	39.179	60.821
4.452	33.142	64.858
3.509	30.133	69.867
18.557	80.295	19.705
14.925	72.739	27.261
12.535	66.776	33.224
10.650	59.608	40.392
8.776	52.868	47.132
6.712	45.317	54.683
..
..

In order to get an idea as to the relative efficiency in salting out power of the various salts employed and also as to the varying effect of individual

salts on different alcohols, four diagrams have been made. Fig. 14 is a comparison of the values obtained with sodium chloride, sodium carbonate, potassium fluoride and potassium carbonate with mixtures of propyl alcohol and water.

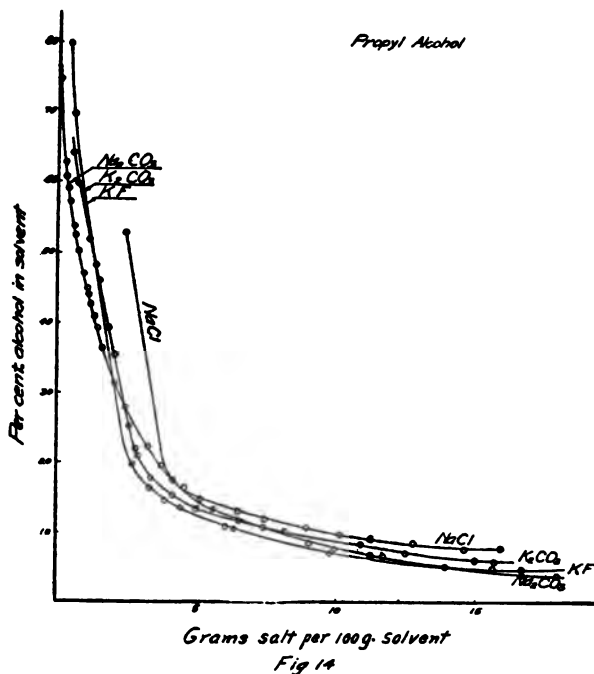


Fig. 15 is a comparison of the same four salts, using allyl alcohol and water as the solvent. In addition, Fig. 15 contains two values for sodium fluoride and four for potassium chloride. These will be discussed later. Fig. 16 is a comparison of solvents from four different alcohols, ethyl, allyl, normal propyl and isopropyl alcohol using a single salt, potassium fluoride. Fig.

17 shows the results with the same four alcohols using potassium carbonate.

The three components are represented in rectangular coordinates by plotting the two liquid components together in one direction and the solid in terms of its ratio to the sum of the two liquids at right angles. Thus a horizontal line at 30% alcohol in the solvent also represents by difference 70% of water in the solvent. All the points plotted represent what might be called "turbidity points," the line connecting the points in any system being the boundary between the homogeneous and heterogeneous systems. To illustrate: Given any solution with a composition represented by any point on any of the lines shown and if its composition be altered by the addition of an infinitesimal amount of the salt, the solution will separate into two phases. In all cases, except the values for allyl alcohol with potassium chloride and sodium fluoride on Fig. 15, these phases are both liquid. In the portions of the curves shown in Figs. 14, 15, 16 and 17 the addition of an infinitesimal amount of the alcohol will effect the same separation into two phases.

One of the most noticeable things in Figs. 14 and 15 is that the order of efficiency in salting out effect, per gram salt in 100 g. solvent, is the same for propyl alcohol as for allyl alcohol in solutions with high alcoholic

content, sodium chloride having the least effect and sodium carbonate the most per weight used.

It has been suggested that the salting out effect of salts on alcohols was largely a matter of the ions present in the solution of the salt. In order to determine whether any such law governed the matter, trials were made using sodium fluoride and potassium chloride with allyl alcohol as these two salts, with the other four used, would give us three potas-

sium salts, three sodium salts, two carbonates, two chlorides and two fluorides—thus completing series which should show any very definite relations if these existed. With both potassium chloride and sodium fluoride results were somewhat undecided, as neither salt gave two liquid phases on addition to an alcohol-water mixture within the limits of composition used in the other curves. However, two phases were easily obtained, one solid and one liquid, which could be made homogeneous

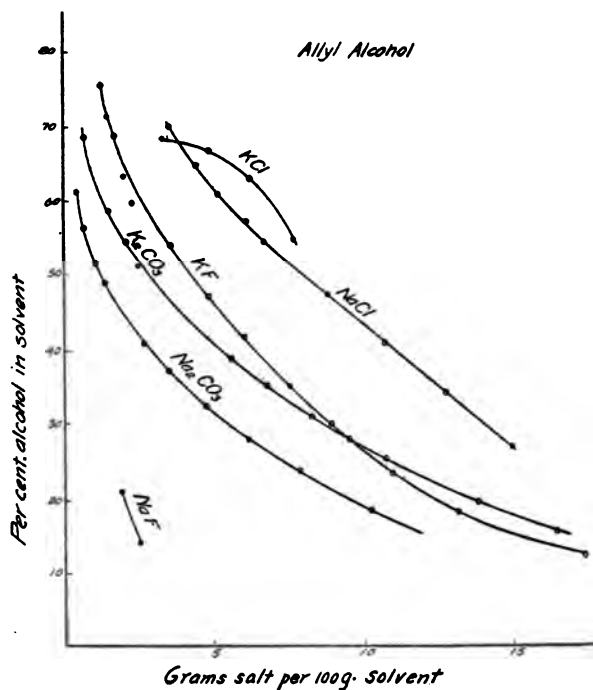
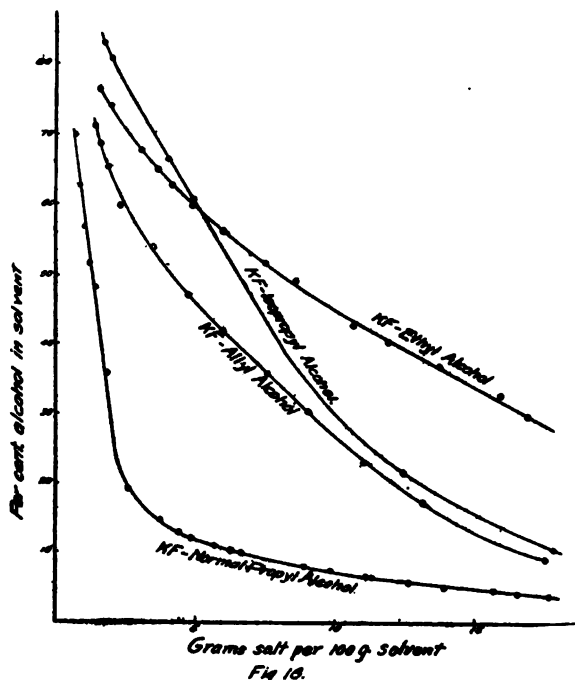


Fig. 15.

by the addition of water and again separated by addition of alcohol or of salt. Thus, while these points measured are real turbidity points, they are not strictly comparable with points on the other curves. However this would not seem to vitiate the conclusions drawn, since the existence of any law correlating solubility and the ions present would apply equally here.

If we examine Fig. 15 for such evidence, we find that it takes less of the sodium salt than of the potassium salt to cause a separation into two phases, whether the salt be the carbonate, the chloride or the fluoride. This, however, may be due as much to the greater weight of the molecule of potassium salt as to the individuality of the ion concerned. If we should express the amount of salt used in terms of gram-molecules or in normality, our curves would not show the same regularity and the



similarity between the order of the salts in Figs. 14 and 15, would disappear entirely.

If we look for a specific effect of the acid ion, in Fig. 15, we get but little encouragement. It requires less of the fluorides to salt out the alcohol than of the corresponding chlorides,—but when we compare the fluorides with the carbonates, we see that, while it takes less of the sodium fluoride than of the sodium carbonate to cause a separation into two phases, it requires more of the potassium

fluoride than of the potassium carbonate.

Attention should be called to the fact that while many of the curves seem to approach as the alcoholic content decreases, in reality they usually diverge, for the difference in salt content of limiting homogeneous solutions containing solvents of like composition is measured by horizontal distances between parallel curves and not by perpendicular distances.

A comparison of Figs. 16 and 17 shows at once a striking similarity. Through a large portion of their length the order is the same for the different alcohols in the case of the dehydration with potassium fluoride as with potassium carbonate. The position and the slope both give the same average values. This makes it clear that the salting out effect of salts on water-alcohol mixtures is dependent largely on the individuality of the alcohol used and that differences are fairly constant with changing salts. When we seek the reason for the differences in the curves of the various alcohols with a single salt, the most noticeable fact is the great difference in the values for the isomeric propyl alcohols. None of the alcohols investigated show great differences than these two and it is at once plain that there is no additive property involved. The two curves showing the most similarity are those for allyl and isopropyl alcohol in both Fig. 16 and Fig. 17. This in spite of the fact that this pair shows the most dissimilarity, chemically, of any of the possible six pairs present. Normal propyl alcohol and ethyl alcohol are most similar chemically.

and while there is some slight resemblance between their curves as shown in Figs. 16 and 17, it is not pronounced and the differences in the amounts of salt present necessary to cause a separation into two layers is very great, and becomes increasingly so as we increase the amount of water present in solutions of both. This is especially evident if we note the horizontal distances between the two curves.

Summary.

Seven new systems have been investigated and curves plotted, namely:

Normal propyl alcohol-sodium carbonate-water;

Isopropyl alcohol-potassium fluoride-water;

Isopropyl alcohol-potassium carbonate-water;

Allyl alcohol-potassium fluoride-water;

Allyl alcohol-potassium carbonate-water;

Allyl alcohol-sodium carbonate-water;

Allyl alcohol-sodium chloride-water.

Potassium fluoride was found to be the most satisfactory of the dehydrating agents employed, especially when the object was the determination of the water content of the alcohol, on account of the ease with which the end point could be determined with widely varying composition of solvent, on account of the fact that it caused a separation into two phases only and those both liquid phases over a relatively large range in composition of solvent and on account of the large amount of water with which it combines to form its lowest hydrate. Potassium carbonate was found to work very satisfactorily for all of the alcohols studied.

Curves have been worked out for the determination of the water content of allyl alcohol and of isopropyl alcohol by the method used and recommended by Frankforter and Frary for ethyl and normal propyl alcohols.

No evidence was found relating the salting out effect to the chemical

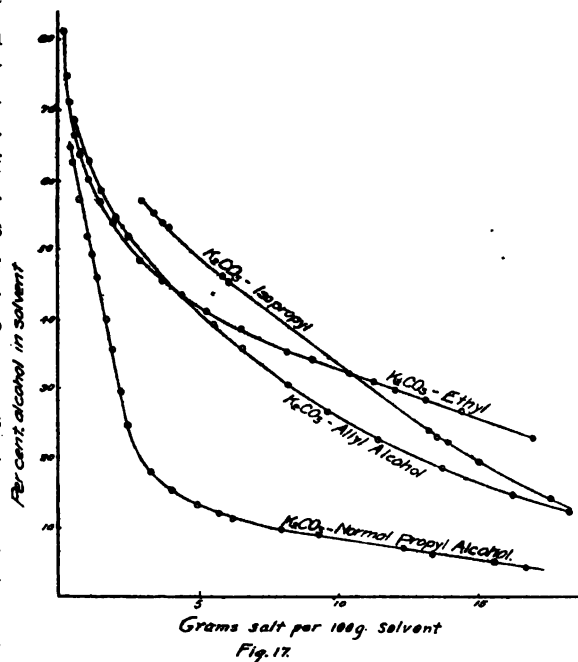


Fig. 17.

constitution of the salts or of the alcohols. The salting out efficiency of a salt seems rather to be a function of its solubility in the water and in the alcohol, of the amount of water with which it unites to form its lowest hydrate, and of the ability of the alcohol to replace the water of hydration.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

PHENYL ESTERS OF OXALIC ACID.

By ROGER ADAMS AND H. GILMAN.

Received August 12, 1915.

Introduction.

In the course of a research in this laboratory, we desired to use one of the substituted phenyl esters of oxalic acid. In reviewing the methods already available for the preparation of these substances, we found them to be few in number, limited in applicability and not suited to the preparation of the particular compound wanted. Nencki¹ first prepared the phenyl ester of oxalic acid by boiling phosphorus oxychloride with anhydrous oxalic acid and phenol. This method was extended by Bischoff² to the preparation of substituted phenyl esters of oxalic acid, and was shown by him to work well with certain types of substituted phenols. With many phenyl derivatives, however, only small yields of esters could be thus produced, and in several cases the esters, if they were formed at all, could not be isolated from the reaction mixtures. Thus, *e. g.*, the cresols, xylenols and carvacrol gave good results, thymol, *p*- and *m*-nitrophenols gave very poor yields, while the desired products from the *o*-nitrophenol, α - and β -naphthols, could not be obtained. Moreover, this method cannot be applied to any phenol containing a substituting group which is sensitive to hot phosphorus oxychloride.

A second method was used by Bischoff³ for the preparation of this class of compounds. It consisted in heating the phenyl ester of oxalic acid with the substituted phenol, when replacement occurred and the substituted phenyl ester resulted. This gave poor results, but was applicable to a number of esters which could not be made by the first process. The α - and β -naphthyl esters are examples.

In the manufacture of aurin, from phenol, oxalic acid and sulfuric acid, a by-product was obtained which Claparède and Smith believed to be the phenyl ester of ortho-oxalic acid.⁴ This they also synthesized by distilling a mixture of oxalic acid and phenol, or by simply dissolving phenol

¹ *J. prakt. Chem.*, [2] 25, 283 (1882).

² *Ber.*, 35, 3440 (1902).

³ *Ibid.*, 35, 3441, 3448 (1902).

⁴ *J. Chem. Soc.*, 43, 358 (1883).

and anhydrous oxalic acid in glacial acetic acid and heating.¹ The corresponding α - and β -naphthyl compounds were also prepared. This method, however, is very limited in application, as shown by Bischoff,² and has no importance in the synthesis of the compounds in question, since water could not be removed to give the phenyl esters of oxalic acid. In fact, Hailer³ has given some evidence that these supposedly ortho-oxalic acid esters are nothing but oxalic acid with two molecules of phenol of crystallization.

This comprises all the work on the synthesis of the phenyl esters of oxalic acid. We have, therefore, looked for a more suitable method of preparation than the one mentioned, and have studied the action of oxalyl chloride on phenols under different conditions. We found that treatment of phenols with oxalyl chloride alone gave poor results, due chiefly to the volatility of the chloride. In the presence of pyridine, however, the reaction ran smoothly, and we were able so to adjust the experimental conditions that it was possible to produce any type of substituted phenyl ester in practically quantitative yields. The general procedure is as follows:

About 25 cc. of pyridine are cooled well in ice and to this 5 g. of pure oxalyl chloride are added slowly. The yellow addition product of the two substances separates instantly in the form of yellow lumps. These are now crushed carefully with a spatula before proceeding further. Two molecules of phenol are dissolved in a few cc. of pyridine, and the solution is added gradually to the oxalyl chloride pyridine compound, then the whole mixture is allowed to stand about two hours, or more, at 0°. To obtain the ester, the reaction product is poured into a mixture of concentrated hydrochloric acid and ice. The pyridine thus goes into solution, and the ester precipitates. It is filtered, washed with water, then (except in the cases when polyphenols and oxyacids have been used) is treated with a cold dilute sodium hydroxide solution to extract any traces of unchanged phenol which may be present. Finally, the ester is filtered again, washed with water, dried, and crystallized.

To get the best results, it is essential to crush well the lumps of the oxalyl chloride pyridine compound, and to keep the reaction mixture at 0° or below. In one or two of the experiments carried out, after putting the substances together, we heated the mixture for a few hours under a reflux condenser. This proved unsatisfactory, however, for, in the first place, blackening and charring took place, as well as the formation of colored by-products, and, secondly, the oxalyl chloride at the high temperature had a greater tendency to act as a dehydrating agent. This

¹ *Ber.*, 17, 1740 (1884).

² *Ibid.*, 35, 3444 (1902).

³ *Chem. Zentr.*, 1910, I, 1039.

latter happened in the case of salicyl aldehyde, no ester being produced. We made a number of experiments also at room temperature, allowing the mixture to stand overnight. Most of the reactions went smoothly, but in one or two instances there was some difficulty. Thus, the salicyl aldehyde gave only a tarry-like mass, and hydroquinone gave a considerable amount of a dehydration product. Besides, small amounts of colored products sometimes formed, which were not too easily removed. Keeping the reaction at 0° , however, gave very satisfactory results, clean, pure compounds, and in all except one or two cases practically quantitative yields of the esters.

We chose for experimentation different types of substituted phenols, not only such as had already been used, but also others, more particularly some containing substituting groups sensitive to phosphorus oxychloride.

Experimental.

Of the following compounds prepared, the di-*p*-cresyl, diguaiacyl, di- α -naphthyl, and di- β -naphthyl esters of oxalic acid had already been synthesized by Bischoff, using other methods. In every case, our compounds agreed with his in solubility, and when crystallized from the same solvent agreed also in crystalline form. We found the melting point of the di-*p*-cresyl ester to be 147° , and of the di- β -naphthyl ester to be 188° as compared with Bischoff's 149° for the former and 191° for the latter. The other two had the same melting point.

I. Monatomic Phenols.

(a) Hydrocarbon Substituting Groups.

1. **Di-*p*-cresyl Ester of Oxalic Acid,**¹ $(\text{CH}_3\text{-C}_6\text{H}_4)_2\text{C}_2\text{O}_4$.—Shiny white plates from a mixture of equal parts of alcohol and ether. M. p. 147° .

Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_4$: C, 71.1; H, 5.2. Found: C, 71.0; H, 5.3.

2. **Di- α -naphthyl Ester of Oxalic Acid,**¹ $(\text{C}_{10}\text{H}_7)_2\text{C}_2\text{O}_4$.—Silky needles from benzene or glacial acetic acid. M. p. $161\text{--}162^{\circ}$.

Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_4$: C, 77.2; H, 4.1. Found: C, 77.1; H, 4.3.

3. **Di- β -naphthyl Ester of Oxalic Acid,**² $(\text{C}_{10}\text{H}_7)_2\text{C}_2\text{O}_4$.—If the material obtained by following the general directions given was crystallized from benzene, it formed tiny, white lumps. M. p. $146\text{--}147^{\circ}$. On analysis this substance proved to be a molecular compound of the di- β -naphthyl ester and one molecule of benzene. It was extremely stable, for heating at $80\text{--}90^{\circ}$ for several hours did not decompose it.

Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_4\text{-C}_6\text{H}_6$: C, 80.0; H, 4.8. Found: C, 79.4; H, 5.0.

By crystallizing the above substance from glacial acetic acid, however, the benzene was driven out, and the free ester formed tiny, white needles. M. p. $188\text{--}189^{\circ}$.

¹ *Ber.*, 35, 3443 (1902).

² *Ibid.*

Calc. for $C_{22}H_{14}O_4$: C, 77.2; H, 4.1. Found: C, 77.3; H, 4.3.

(b) *Other Substituting Groups.*

1. **Di-*o*-nitrophenyl Ester of Oxalic Acid**, $(NO_2-C_6H_4)_2C_2O_4$.—Long, flat, yellow needles from benzol. M. p. 185° . Soluble in chloroform, glacial acetic acid; very slightly soluble in ethyl alcohol and methyl alcohol; insoluble in ether.

Calc. for $C_{12}H_6O_8N_2$: C, 50.6; H, 2.4. Found: C, 50.9; H, 2.6.

2. **Di-salicyl Aldehyde Ester of Oxalic Acid**, $(CHO-C_6H_4)_2C_2O_4$.—Shiny, white plates from benzene. M. p. $153-154^\circ$. Soluble in chloroform and glacial acetic acid; slightly soluble in ethyl alcohol, methyl alcohol; insoluble in ether.

Calc. for $C_{16}H_{10}O_6$: C, 64.4; H, 3.4. Found: C, 64.5; H, 3.5.

If the reaction of oxalyl chloride, pyridine, and salicyl aldehyde was carried on at the boiling temperature of the pyridine, none of the above ester formed, but a considerable amount of a white solid was isolated from the black reaction mass. This crystallized from ether, melted at 129° , and on analysis proved to be the well-known di-salicyl aldehyde.

Calc. for $C_{16}H_{10}O_6$: C, 74.3; H, 4.4. Found: C, 74.1 and 74.4; H, 4.8 and 4.6.

At room temperature the salicyl aldehyde gave no ester, just a reddish, sticky product.

3. **Di-vanillin Ester of Oxalic Acid**, $[(CH_3O)(CHO)C_6H_3]_2C_2O_4$.—Very small, white crystals from glacial acetic acid. Melting point $203-204^\circ$. Soluble in chloroform and benzene. Very slightly soluble in ethyl alcohol and methyl alcohol. Insoluble in ether.

Calc. for $C_{18}H_{14}O_8$: C, 60.3; H, 3.9. Found: C, 59.9; H, 3.9.

4. **Di- β -aceto- α -naphthyl Ester of Oxalic Acid**, $(CH_3CO-C_{10}H_7)_2C_2O_4$.—Small, white, leaf-like crystals from benzene. M. p. 197° . Readily soluble in glacial acetic acid, chloroform and acetone. Slightly soluble in ethyl alcohol, methyl alcohol, and ether.

Calc. for $C_{28}H_{18}O_6$: C, 73.2; H, 4.2. Found: C, 73.0; H, 4.4.

5. When we attempted to prepare the salicylic acid ester of oxalic acid, the reaction apparently ran smoothly, and a good yield of a white solid resulted. However, we were unable to find a solvent for the substance, and on testing we found nitrogen. This was undoubtedly the pyridine salt of the di-salicylic acid ester of oxalic acid which had not decomposed on treatment with strong hydrochloric acid. By the action of hot concentrated hydrochloric acid or sodium hydroxide, the pyridine was set free, but the ester hydrolyzed at the same time, so that only complete decomposition products resulted.

6. **Di-methyl Salicylate Ester of Oxalic Acid**, $(CH_3OOC-C_6H_4)_2C_2O_4$.—White needles from benzene. M. p. 158° . Readily soluble in ethyl

alcohol, chloroform, benzene, glacial acetic acid; slightly soluble in methyl alcohol.

Calc. for $C_{18}H_{14}O_4$: C, 60.3; H, 3.9. Found: C, 60.0; H, 3.9.

7. **Di-guaiacyl Ester of Oxalic Acid**,¹ $(CH_2O-C_6H_4)_2C_2O_4$.—Shiny, white plates from a mixture of alcohol and ether. M. p. 127°.

Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.6. Found: C, 63.8; H, 4.9.

II. Diatomic Phenols.

(a) **Di-*p*-hydroxyphenyl Ester of Oxalic Acid**, $(HO-C_6H_4)_2C_2O_4$.—As precipitated from the reaction mixture, this substance formed a white powder, only very slightly soluble in all the common solvents, or even heavier solvents, such as glacial acetic acid, anisol or benzyl alcohol. It started to shrink at 192° and melted at 212°. The compound was prepared for analysis by washing well with cold water, then several times with hot benzene. It was soluble with a yellow color in dilute sodium hydroxide.

Calc. for $C_{16}H_{12}O_6$: C, 61.3; H, 3.6. Found: C, 60.9; H, 3.8.

If the hydroquinone was added to the oxalyl chloride pyridine compound at room temperature, and the mixture allowed to warm up from the heat of reaction, then a mixture of compounds resulted from which one could be obtained by the action of glacial acetic acid. This crystallized in white needles from glacial acetic acid and melted at 226°. The analysis agreed well for the monoacetate of di-*p*-oxyphenyl ether. As the production of this compound was rather uncertain, and as we obtained but poor yields of it, we have not studied it further. Slightly soluble in ethyl and methyl alcohol, chloroform, ether, benzene.

Calc. for $C_{14}H_{12}O_4$: C, 68.8; H, 4.9. Found: C, 68.9; H, 4.7.

CAMBRIDGE, MASS.

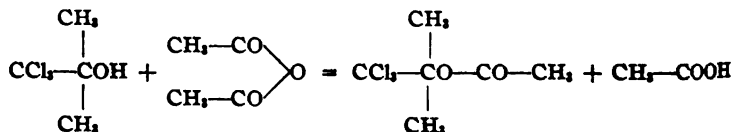
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & Co.]

MONO-ACETYL-TRI-CHLOROTERTIARY-BUTYL-ALCOHOL (ACETYL CHLORETONE.)

By T. B. ALDRICH.

Received September 13, 1915.

When trichlorotertiary-butyl-alcohol (presumably tri-bromotertiary-butyl-alcohol acts in the same way) is acetylated in the usual manner with acetic anhydride and anhydrous sodium acetate, an acetyl compound is formed according to the following equation:



¹ Ber., 35, 3443 (1902).

Preparation.—One (1) part of chloretonone was boiled with two (2) parts of acetic anhydride and one (1) part of anhydrous sodium acetate for two hours, using a reflux condenser. The solution, after cooling and diluting with water, was neutralized with sodium carbonate and subjected to steam distillation, the acetyl derivative passing over with the steam in the form of an oil that was practically colorless. The oil was collected with ether, the ethereal solution washed with water, then dried with calcium chloride, and finally filtered through a dry filter into a tared vessel. After evaporating the ether the residual oil gave, in one instance, a yield of about 80%. Slight decomposition took place when the oil was distilled at ordinary temperature; however, the greater part went over between 180–190° as a nearly colorless oil. When distilled in partial vacuum at 246 mm. the substance boiled fairly constant without any apparent decomposition at 145–146° and gave a yield of 85% of the amount started with. Chloretonone under the same conditions (pressure, etc.) boils at 134–136°.

Combustion and chlorine determinations were made with a product, boiling at 151–153° under 250 mm. pressure. The bulb for holding the liquid for analysis was weighed empty, then warmed, and the neck of the bulb which had been drawn to a fine tube immersed in the acetyl chloretonone. When, on cooling, sufficient oil had entered the bulb, it was reweighed.

The analytical results for carbon were somewhat lower and for chlorine somewhat higher than the calculated values, indicating the presence of some unchanged chloretonone. This was verified by the results of the purification treatment.

In order to remove traces of chloretonone, the acetyl compound already analyzed was heated on the steam bath for 20 min. with 100 cc. of a 10% NaOH solution in order to decompose the chloretonone present. The acetyl derivative, which was unaffected by this treatment, was then collected with ether, washed, dried, and distilled in the usual manner under reduced pressure. The substance distilled at 151–152° under a pressure of 237 mm. The following chlorine determination (Carius) is sufficient to show that this compound is practically pure.

0.3831 g. gave 0.7535 g. AgCl or 0.1864 g. Cl.

Calc. for $C_6H_9O_2Cl_3$: 48.63%. Found: 48.65%.

Three cc. of the acetyl compound were placed in a pressure tube with 10 cc. of H_2O and heated for 3 hours at 160°. On opening the tube there was no apparent change. On heating the resealed tube for 3 hours at 250° complete decomposition of the substance took place, and on opening the tube there was considerable pressure. The substance was in part carbonized but there was no evidence of chloretonone, the reaction of the liquid was acid and $AgNO_3$ gave a precipitate soluble in NH_4OH .

Two cc. of the acetyl compound were placed in a sealed tube with 25 cc. H_2O and heated to 160° for 8 hours. On opening the tube, there was considerable pressure, and a reddish brown oil was noticed ($1\frac{1}{2}$ cc.) at the bottom of the tube, the supernatant liquid being slightly yellow. Its reaction was strongly acid and $AgNO_3$ gave a voluminous precipitate soluble in NH_4OH .

When boiled with water for a long time (108 hours), using a reflux condenser, some crystals resembling chloretone were observed in the condenser and neck of the flask (that is, on standing overnight). These were collected on a filter, dissolved in dilute alcohol and recrystallized. White needles; taste and smell like chloretone. M. p. 78° .

When acetyl chloretone is boiled with water to which H_2SO_4 has been added, the saponification takes place much more rapidly. Boiling 7 hours is sufficient to obtain considerable chloretone in the condenser tube.

Although saponification takes place slowly by boiling with water, or water and dilute acids, it is extremely interesting to note that saponification takes place very rapidly when the ester is boiled with an excess (three or four times its volume) of *concentrated* nitric acid. Indeed, after boiling only a few minutes a large amount of chloretone may be thrown out of the acid solution in a crystalline form by the addition of water.

The solubilities of the acetyl ester are practically the same as those of chloretone. It dissolves very readily in alcohol, acetone, ether, chloroform, benzene, etc., and is *practically insoluble* in water, even less soluble than chloretone. (Upon placing 0.5 g. in 100 cc. measuring flask and adding water to mark, very little, if any, passed into solution after shaking occasionally for several days.)

It is volatile, though less so, than chloretone.

(1) 1 cc. was placed on watch glass and allowed to stand at room temperature; at the end of 14 hours $1\frac{1}{2}$ had evaporated.

(2) 1 cc. was placed in an incubator at 37° ; at the end of 14 hours it had evaporated completely.

Acetyl chloretone has anesthetic properties similar to chloretone and brometone; but, since it is so slightly soluble in water, its effect does not appear for several hours, and therefore it cannot be used to advantage as a substitute for chloretone for inducing general anesthesia in animal experiments. On account of its more agreeable odor, it might be used in some instances to advantage in place of chloretone. The toxicity of the acetyl ester, when introduced subcutaneously into guinea pigs is slightly less than that of chloretone; its bactericidal efficiency was not tested.

It is generally accepted that the esters of the tertiary alcohols, on

heating alone above their boiling point in a sealed tube, are decomposed into acids and unsaturated hydrocarbons,¹ and we might expect a similar behavior in the case of acetyl-trichloro-tertiary-butyl-alcohol when heated similarly. The decomposition products of acetyl chloretone when heated *alone* were not determined, but with water or acids it gave rise, in part as far as could be observed, to chloretone without the above decomposition.

DETROIT, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 255.]

THE SYNTHESIS OF CERTAIN SUBSTITUTED SYRINGIC ACIDS.

BY MARSTON TAYLOR BOOERT AND EDWARD PLAUT.²

Received October 14, 1915,

Introductory.

Over a century ago, Braconnot³ undertook an examination of various plants with particular reference to the acids they contained. Among the plants studied was the common lilac (*Syringa vulgaris*), and he called attention to the presence therein of a bitter substance, precipitable by basic lead acetate, the nature of which was not determined.

Since this early research, various chemists have made the lilac the subject of their investigations. In 1823, Robinet and Petroz⁴ examined the seeds and capsules, and found therein a saccharin principle, later shown to be mannite,⁵ and a bitter principle; but failed to isolate the latter in sufficient amount or purity to determine its nature.

Fifteen years later, Favrot⁶ recovered an oil from the flowers.

In 1841, Bernays⁷ obtained from the bark, and also from the leaves and green twigs, a crystalline substance which he believed to be analogous to salicin and phloridzin and therefore termed "syringin." At about the same time, Meillet⁸ reported the discovery, in the leaves and green seed capsules, of a crystalline substance which he designated "lilacine." Bernays' article appeared in abstract in Liebig's *Annalen*⁹ under the

¹ Lassar-Cohn, "Arbeits methoden," 3d. ed., p. 1152.

² The experimental work upon which this paper is based was submitted by Mr. Edward Plaut in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.

³ *Ann. chim. phys.*, 70, 281-5 (1809).

⁴ *J. Pharm.*, 9, 474 (1823); 10, 139-57 (1824).

⁵ Ludwig, *Archiv. Pharm.*, [2] 91, 289-96 (1857); Kromayer, *Ibid.*, 109, 18, 216 (1862).

⁶ *J. chim. med.*, 14, 212 (1838).

⁷ Buchner's *Repert. d. Pharm.*, [2] 24, 349 (1841); *J. pharm. chim.*, [3] 1, 27 (1842).

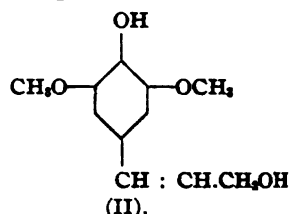
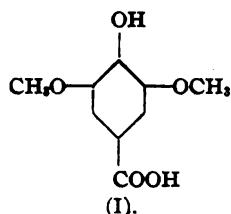
⁸ *J. pharm. chim.*, [3] 1, 25 (1842).

⁹ *Ann.*, 40, 320 (1841).

heading "Lilacin," and in Erdmann's Journal¹ under the caption "Syringin."

It appears to have been first suggested by Reinsch² that syringin was identical with the "ligustrin" discovered by Polex³ in the bark of the privet (*Ligustrum vulgare*); and this surmise was later shown to be correct by the work of Kromayer.⁴ It is of interest to note that, in the case of the privet also, the syringin (ligustrin) is accompanied by mannite.⁵ Kromayer also discovered that syringin could be hydrolyzed to glucose and "syringenin." Further, he observed in the leaves and half-ripe fruit of the lilac a noncrystalline bitter substance, "syringopikrin," which likewise appears to be a glucoside.

Following Kromayer's investigations, Koerner⁶ took up the study of syringin. His analyses established its empirical composition as $C_{17}H_{24}O_9 + H_2O$, and therefore that of syringenin as $C_{11}H_{14}O_4$. Oxidation with potassium permanganate, converted syringin into glucosyringic acid which, on hydrolysis, yielded glucose and "syringic acid." After a careful study of the latter acid and various of its derivatives, Koerner concluded that it must possess Formula I, and that syringin is therefore the glucoside of an alcohol of Formula II (sinapinic alcohol):



Subsequent work by other investigators has fully corroborated these deductions.⁷

The researches of Power⁸ indicate that syringin, and possibly also glucosyringic acid, are present in the bark of *Robinia pseudacacia*.

In addition to syringic acid itself, its barium, zinc and copper salts, and its methyl ester, sundry derivatives and condensation products are mentioned in the literature.

¹ *J. prakt. Chem.*, [1] 25, 121 (1842).

² *Jahrb. prakt. Pharm.*, 16, 389-93 (1848).

³ *Archiv. Pharm.*, [2] 17, 75-8 (1839).

⁴ *Ibid.*, [2] 109, 18, 216 (1862); 113, 19 (1863).

⁵ Kromayer, *Archiv. Pharm.*, [2] 101, 281-4 (1860).

⁶ *Gazz. chim. ital.*, 18, 209-19 (1888).

⁷ Gadamer, *Ber.*, 30, 2330 (1897); *Archiv. Pharm.*, 235, 570 (1897); Graebe and Martz, *Ber.*, 36, 216, 1031 (1903); *Ann.*, 340, 220 (1905); Graebe and Hess, *Ann.*, 340, 235 (1905); Mauthner, *J. prakt. Chem.*, [2] 82, 271 (1910); 84, 142 (1911); *Ann.*, 395, 273 (1913); *J. prakt. Chem.*, [2] 91, 179 (1915); Bogert and Isham, *This Journal*, 36, 519 (1915); *et al.*

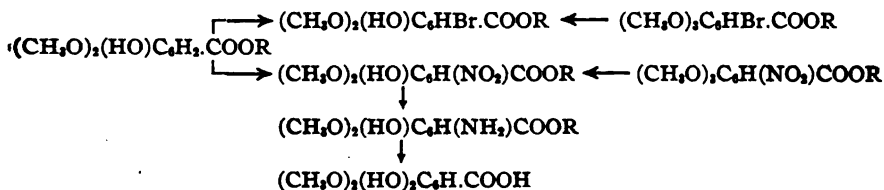
⁸ *Pharm. J.*, 1901, 275.

As yet, nothing appears to have been done in the direction of preparing and studying the substitution products of this interesting acid. We have thought it desirable, therefore, to undertake an investigation along these lines, not only because of our ignorance of such substances, the accessibility of the initial material, and the occurrence of syringic compounds in nature; but also in the hope that it might open a way to the synthesis of other natural products or of compounds closely allied to them.

The subjoined experiments represent the beginning of this work, and may be summarized as follows:

Syringic acid, prepared from trimethylgallic acid by the method of Bogert and Isham,¹ was changed to its methyl ester and the acetyl derivative prepared from the latter.

From methyl syringate were obtained also the monobromo and mononitro derivatives, by reduction of the latter the corresponding amino derivative, and from the amino the hydroxy syringic acid (2,4-dihydroxy-3,5-dimethoxybenzoic acid). The bromo and nitro syringic derivatives were also produced by partial demethylation of the corresponding trimethylgallic compounds:



Methyl bromotrimethylgallate is recorded in the literature² as an oil, boiling at 202° under a pressure of 16 mm. We have succeeded in obtaining it as a colorless crystalline solid, melting at 90°, and in improving the method of producing it.

By the action of nitric acid upon free syringic acid, the hitherto unknown 3,4-dinitropyrogallol-2,6-dimethyl ether was secured.

Diacetyl derivatives of both the amino and hydroxy syringic acid were prepared and studied.

The work is being continued; particularly along lines leading to the production of the apionol ethers, and to the various condensation products obtainable from the amino and hydroxy syringic acids, since one of these latter acids is of anthranilic and the other of salicylic type.

Experimental.

I. Trimethylgallic Derivatives.

Methyl Trimethylgallate, $(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2.\text{COOCH}_3$, was prepared from

¹ *Loc. cit.*

² Hamburg, *Monatsh.*, 19, 596 (1898).

trimethylgallic acid, methyl alcohol and dry hydrogen chloride, as described by Bogert and Isham.¹ As first recorded by Powers and Moore,² it melts at 84° (corr.) and is volatile with steam.

Methyl Bromotrimethylgallate, $(\text{CH}_3\text{O})_3\text{C}_6\text{HBr.COOCH}_3$, has been prepared by Hamburg³ by the action of bromine upon methyl trimethylgallate in carbon tetrachloride solution, as an oil, b_{18} 202°, as mentioned above. On repeating Hamburg's process, our results were similar, the product being a pale yellow oil. We have succeeded, however, in bringing this oil to crystallization and, on recrystallization from ether, obtained it in practically colorless prismatic crystals, melting at 90° (corr.).

More satisfactory results were realized by carrying out the bromination in acetic anhydride solution. Ten grams of methyl trimethylgallate were dissolved in 60 g. acetic anhydride, the flask placed in a freezing mixture and a solution of 13 g. bromine in 60 cc. acetic anhydride run in gradually with constant stirring.⁴ The reaction was allowed to continue for 24 hours, after which the acetic anhydride was removed by distillation under reduced pressure and the residue crystallized from ether. Nearly colorless crystals resulted, melting at 90° (corr.).

Subs. 0.4942, 0.1850: AgBr, 0.2849; CO_2 , 0.2951; H_2O , 0.0719. Calc. for $\text{C}_{11}\text{H}_{13}\text{O}_6\text{Br}$: Br, 26.22; C, 43.29; H, 4.26. Found: Br, 26.27; C, 43.51; H, 4.32.

A cryoscopic molecular weight determination in benzene solution, gave the figure 309, while that calculated is 305.

Methyl Nitrotrimethylgallate, $(\text{CH}_3\text{O})_3\text{C}_6\text{H}(\text{NO}_2).\text{COOCH}_3$.—Schiffer,⁵ Thomas and Siebeling,⁶ and Harding,⁷ have shown that the nitration of free trimethylgallic acid by nitric acid alone, or in the presence of acetic acid, results mainly in the displacement of the carboxyl by the nitro group, with formation of 5-nitro and 5,6-dinitropyrogallol trimethyl ethers, together with but small amounts of nitrotrimethylgallic acid. In our own experiments upon trimethylgallic acid with nitric acid, in acetic acid solution, the dinitropyrogallol trimethyl ether proved to be the chief product. This ether melts at 118.4° (corr.).

Schiffer records that on nitrating ethyl triethylgallate with nitric acid, in glacial acetic solution, he obtained the corresponding mononitro derivative in fine needles, m. p. 104°; but that the action of nitric acid alone upon this, even in the cold, tended to change it to dinitropyrogallol triethyl ether.

¹ THIS JOURNAL, 36, 518 (1914).

² J. Chem. Soc., 95, 254 (1909); see also Bogert and Isham, *Loc. cit.*

³ *Loc. cit.*

⁴ In all halogenations involving the use of free halogens in acetic anhydride solution, the unprotected hand should never be exposed over the surface of the mixture, or serious poisoning may result. Compare Bogert, THIS JOURNAL, 29, 239 (1907).

⁵ *Ber.*, 25, 721 (1892).

⁶ *Ibid.*, 44, 2115 (1911).

⁷ J. Chem. Soc., 99, 1585 (1911).

nitrotrimethylgallate in acetic anhydride solution at low temperature, and obtained the mononitro trimethylgallate in pale yellow crystals, m. p. 27°. Zollik and Feidischewski prepared ethyl ester of nitrotrimethylgallate and yellowish nitrated methyl triacrylate in similar manner. Thomas and Siebeling discovered that they obtain either mono- or dinitro derivatives according to temperature of the reaction. Power and Shedden found that they nitrated which ethyl triacrylgallate, they obtained ethyl dinitroacrylgallate, which could be converted into the triacetyl derivative by action of acetic anhydride, or into dinitroacrylgallate by hydrolysis with sulfuric acid.

own experience in nitrating methyl trimethylgallate with nitric acid, or in the presence of acetic acid, either cold or at 100°, was considerable gave but small yields of the desired nitro ester, together with much most convenient to prepare the methyl nitrotrimethylgallate in 120 cc. of acetic anhydride, either cold or at 100°, was found in a same way as Hamburg, operating as follows: 30 g. of methyl trimethylgallate and 21 cc. of nitric acid (1 cc. of concentrated) added very slowly with constant stirring into a freezing mixture and 21 cc. of acetic anhydride was then distilled off at first brownish and hot, on standing over with stirring into a flask was dissolved in 25 cc. of alcohol, and the tarry residue was separated by filtration. The crude product was purified by solution in alcohol or ether, and then melted in a water bath. The product was purified by reduction with iron and hydrochloric acid, and the free amino acid was obtained by reprecipitation from the solution in alcohol or ether, and then melted in a water bath. The product was purified by reduction with iron and hydrochloric acid, and the free amino acid was obtained by reprecipitation from the solution in alcohol or ether, and then melted in a water bath.

Calc. for $(C_6H_5O)_3C_3H_4N$: C, 60.1%; H, 3.1%; N, 3.8%. Found: C, 59.8%; H, 3.2%; N, 3.7%.
Calc. for $(C_6H_5O)_3C_3H_4N$: C, 60.1%; H, 3.1%; N, 3.8%. Found: C, 59.8%; H, 3.2%; N, 3.7%.

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by neutralization with sodium carbonate solution and extraction with ether. The purified ester melted at 41° (corr.).

II. Syringic Derivatives.

Syringic Acid, $(\text{CH}_3\text{O})_2(3,5)(\text{HO})(4)\text{C}_6\text{H}_2\text{COOH}(1)$.—The syringic acid used in the following experiments was prepared from trimethylgallic acid and fuming sulfuric acid, by the method of Bogert and Isham,¹ which gives large yields readily and rapidly. The yield of pure acid occasionally ran as high as 98%, and actually averaged about 92% for something over 50 experiments.

The purified product formed colorless crystals, melting at 204° (corr.), in agreement with that found by Graebe and Martz,² and by Bogert and Isham;¹ and was soluble in chloroform, ether, alcohol, or hot water; difficultly soluble in cold water. With ferric chloride solution, it gave a reddish brown coloration, as observed by Power³ and by Graebe and Martz.⁴ At high temperatures, the acid lost CO_2 , giving 1,3-dimethylpyrogallol;⁵ and, on oxidation with sodium chromate and dilute sulfuric acid, yielded 3,5-dimethoxyquinone.⁶

Subs. 0.2010: CO_2 , 0.4024; H_2O , 0.0949. Calc. for $\text{C}_8\text{H}_6\text{O}_5$: C, 54.54; H, 5.05. Found: C, 54.59; H, 5.22.

The preparation method of Graebe and Martz¹ was also tried, boiling the trimethylgallic acid with excess of concentrated hydrobromic acid (48% aqueous acid), but proved much less satisfactory, as it requires more time and does not give quite as good yields.

The **Methyl Ester** was prepared by the action of dry hydrogen chloride upon a methyl alcohol solution of the acid, as described by Bogert and Isham,¹ and melted $83-4^{\circ}$ (corr.) in the hydrated form, and at $106-7^{\circ}$ (corr.) in the anhydrous state.⁷ It is volatile with steam.

The **Ethyl Ester**, prepared in similar manner, separated from dilute alcohol in colorless crystals, m. p. 55.8° (corr.); soluble in alcohol or ether, difficultly soluble in water. Yield, 85%.

Subs. 0.3322: CO_2 , 0.7145; H_2O , 0.1855. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_5$: C, 58.40; H, 6.19. Found: C, 58.49; H, 6.21.

Isoamyl Ester.—In the preparation of this, concentrated sulfuric acid was used as the condensing agent, and the excess of the alcohol was removed by distillation under reduced pressure. The crude product was

¹ *Loc. cit.*

² *Ann.*, 340, 220 (1905).

³ *Pharm. J.*, 1901, 275.

⁴ *Ber.*, 36, 216 (1903).

⁵ Koerner, *Gazz. chim. ital.*, 18, 209 (1888); Graebe and Hess, *Ann.*, 340, 235 (1905).

⁶ Gadamer, *Ber.*, 30, 2330 (1897); Graebe and Martz, *Ann.*, 340, 220 (1905); Bogert and Isham, *Loc. cit.*

⁷ Graebe and Martz, *Loc. cit.*; Bogert and Isham, *Loc. cit.*

crystallized from ethyl alcohol to constant m. p., and then formed fine, colorless needles, m. p. 101° (corr.).

Subs. 0.2441: CO_2 , 0.5634; H_2O , 0.1537. Calc. for $\text{C}_{14}\text{H}_{18}\text{O}_5$: C, 62.68; H, 7.46. Found: C, 62.95; H, 7.01.

Methyl Acetylsyringate, $(\text{CH}_3\text{O})_2(\text{CH}_3\text{COO})\text{C}_6\text{H}_2\text{COOCH}_3$.—Five g. methyl syringate dissolved in 15 g. acetic anhydride with decided rise of temperature. On standing 24 hours, some crystals separated. These were removed and an additional crop obtained from the mother liquor by dilution with water and warming. The crude product was purified by crystallization from alcohol, and then appeared in colorless crystals, m. p. 129° (corr.), soluble in alcohol, ether, or acetic anhydride (moderately), and practically insoluble in water. Yield over 95%.

Subs. 0.2136: CO_2 , 0.4284; H_2O , 0.1172. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}_5$: C, 52.17; H, 6.08. Found: C, 52.24; H, 6.1.

Methyl Bromosyringate, $(\text{CH}_3\text{O})_2(\text{HO})\text{C}_6\text{HBrCOOCH}_3$.—Attempts to brominate syringic acid directly, in various solvents, proved unsatisfactory. The same was true when an effort was made to brominate methyl syringate in alcohol, ether, chloroform or carbon disulfide solution. On the other hand, when the methyl ester was used in acetic anhydride solution, the reaction proceeded much more smoothly.

Ten g. of the ester, dissolved in 100 cc. of acetic anhydride, were cooled to 0° and treated gradually, with constant stirring, with 12 g. bromine dissolved in 60 cc. of the anhydride. After standing overnight, the excess of anhydride was distilled off under diminished pressure, the residue taken up with ether, the ether solution filtered, the solvent driven off, and the residue crystallized from dilute alcohol. Colorless crystals were obtained, m. p. 89° (corr.); soluble in alcohol, ether or benzene, practically insoluble in cold water.

Subs. 0.5335, 0.2036: AgBr, 0.3360; CO_2 , 0.3054; H_2O , 0.0712. Calc. for $\text{C}_{10}\text{H}_{11}\text{O}_5\text{Br}$: Br, 27.48; C, 41.23; H, 3.78. Found: Br, 27.44; C, 40.91; H, 3.88.

The same substance was prepared by the Graebe and Martz method, heating the methyl bromotrimethylgallate with concentrated (48%) hydrobromic acid. The yield by this method was 40%, and the m. p. of the purified product 89° (corr.). A mixture of this substance with that obtained by the direct bromination method showed no change in the melting point.

The substitution of fuming sulfuric acid for hydrobromic in the above method of preparation proved unsatisfactory, since it caused too much decomposition and carbonization.

Probably for similar reasons, an attempt to apply the Juvalta process¹ to trimethylgallic acid was a failure. As fuming sulfuric acid converts trimethylgallic acid smoothly into syringic, it was thought that it might

¹ D. R. P. 50, 177, *Friedländer*, 2, 93; *Rupp, Ber.*, 29, 1625-34 (1896).

be possible to obtain highly halogenated syringic acids by this process; but the treatment was evidently too severe and decomposition ensued.

3,4-Dinitropyrogallol-2,6-dimethyl Ether, $(\text{CH}_3\text{O})_2(2,6)(\text{HO})(1)\text{C}_6\text{H}(\text{NO}_2)_2(3,4)$.—As has already been pointed out, the direct action of nitric acid upon trimethylgallic acid gives, as the main product, the dinitropyrogallol trimethyl ether.

In the case of syringic acid, the action of nitric acid causes an entirely analogous change, the chief product of the reaction being 3,4-dinitropyrogallol-2,6-dimethyl ether. The nitration was carried out by dissolving the syringic acid in glacial acetic acid, cooling the solution in a freezing mixture, adding concentrated nitric acid gradually with stirring, allowing the mixture to stand for several hours, and then precipitating by dilution with water. On purification, the ether was secured in pale yellow crystals, m. p. 154° (corr.), soluble in various organic solvents or in caustic alkali solutions, but essentially insoluble in water.

Subs. 0.3165; CO_2 , 0.4758; H_2O , 0.1022. Calc. for $\text{C}_{10}\text{H}_8\text{O}_7\text{N}_2$: C, 41.08; H, 3.41. Found: C, 41.0; H, 3.37. Nitrogen found, 8.32; calc., 8.0.

More or less yellowish tar is apt to be formed in all these nitration reactions.

Methyl Nitrosyringate, $(\text{CH}_3\text{O})_2(\text{HO})\text{C}_6\text{H}(\text{NO}_2)\text{COOCH}_3$.—Eighteen grams of methyl syringate were dissolved in 100 cc. of acetic anhydride, and the solution cooled to -5° in a freezing mixture. To this were added, slowly and with constant stirring, 18 cc. of concentrated nitric acid containing a little fuming acid, maintaining the temperature below 0° throughout the operation. On standing in the ice box overnight, the reddish solution became yellow. Alcohol was then added, to convert the excess of anhydride into acetate, and the solution distilled under reduced pressure. The thick oily residue was poured, with constant stirring, into 500 cc. of water. Most of the nitro ester separated in flocculent form, rose to the top of the solution, and was filtered off. That which remained adhering to the sides of the distilling flask was dissolved out with hot alcohol. The aqueous filtrate from the precipitated nitro ester was concentrated, the alcoholic washings from the flask added, the mixture boiled for a short time, poured hot into 250 cc. of water and the solution saturated with salt. The rest of the nitro ester then separated and was filtered off. Neutralization with sodium carbonate was not found necessary.

Recrystallized from dry benzene or from absolute alcohol, the pure substance appeared in pale yellow, transparent crystals, m. p. 68.3° (corr.). Yield, 75 to 80%.

Subs. 0.2348; CO_2 , 0.4031; H_2O , 0.0914. Calc. for $\text{C}_{10}\text{H}_{11}\text{O}_7\text{N}$: C, 46.69; H, 4.28. Found: C, 46.82; H, 4.33. Nitrogen found, 5.53; calc., 5.47.

The same product was obtained by heating methyl nitrotrimethylgallate with concentrated (48%) hydrobromic acid. It melted at 68° (corr.).

and no material change in the m. p. occurred when this product was mixed with some of that from the direct nitration method. The yield by this HBr method was about 30%.

As already noted, the action of nitric acid alone, or in the presence of acetic acid, upon methyl syringate, results in the formation of considerable yellowish tar and but small yields of the nitro ester.

The **Ethyl Ester**, prepared in an analogous manner, crystallizes from ligroin in nearly colorless, silky needles, m. p. 74° (corr.); soluble in alcohol, ether, ligroin or benzene; and practically insoluble in water.

Subs. 0.3112: CO_2 , 0.5485; H_2O , 0.1344. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_7\text{N}$: C, 48.70; H, 4.78. Found: C, 48.66; H, 4.80.

Methyl Aminosyringate, $(\text{CH}_3\text{O})_2(\text{HO})\text{C}_6\text{H}(\text{NH}_2)\text{COOCH}_3$.—Ten grams methyl nitrosyringate were moistened with alcohol, and 15 g. purified tin and 50 cc. concentrated (33%) hydrochloric acid added. The flask containing the mixture was immersed in cold water until the initial vigorous reaction had somewhat abated, after which the reduction was completed by heating at 100° until the tin was all dissolved. On cooling, the double tin salt of the amino ester separated in pale yellow crystals which were filtered out, washed, suspended in dilute hydrochloric acid, and de-tinned by a current of hydrogen sulfide. The filtrate from the tin sulfide was concentrated under reduced pressure, and the concentrated solution placed in a desiccator over sulfuric acid. Colorless needles of the amino ester hydrochloride separated, m. 192° (corr.); soluble in water, but practically insoluble in neutral organic solvents.

The free amino ester was recovered from its hydrochloride by (1) repeatedly boiling down its aqueous solution, the hydrochloric acid distilling off with the steam, and water being added from time to time; (2) by neutralizing its aqueous solution with sodium carbonate and extracting with ether; or (3), best, by precipitating the aqueous solution of the hydrochloride with ammonium hydroxide solution, the amino ester separating as a colorless precipitate, easily filtered out and dried. Exposed to light and air, it first turns yellow and then gradually browns. Yield, 65%. Recrystallized from dilute alcohol, in the dark, colorless crystals were secured, m. 110° (corr.).

Calc. for $\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}$: C, 52.9; H, 5.7; N, 6.25. Found: C, 52.9; H, 5.98; N, 6.16.

Diacetyl Derivative.—In the first experiment, 3 g. of methyl aminosyringate hydrochloride were dissolved with 1.5 g. fused sodium acetate in 15 cc. acetic anhydride and 5 cc. glacial acetic acid, and the mixture left overnight. Water (50 cc.) was then added, and the mixture warmed for a few minutes on the water bath. This caused it to cloud, and upon cooling colorless crystals separated, which were filtered out and purified by recrystallization from ethyl acetate.

In the second experiment, 3 g. of methyl aminosyringate were warmed

with 15 cc. of acetic anhydride and 0.5 g. fused sodium acetate, and the solution set aside overnight. Water (100 cc.) was then added, and the mixture warmed for a few minutes on the water bath. The solution became cloudy, but settled well upon the addition of a little more sodium acetate. The separated crystals were filtered out, dried, and recrystallized from alcohol. Yield, 4.7 g.

The pure substance forms large, colorless crystals, m. p. 139.9° (corr.); soluble in alcohol or ether.

Better yields were realized from the free amino ester than from its hydrochloride.

Subs. 0.2050: CO₂, 0.4042; H₂O, 0.1034. Calc. for C₁₆H₁₇O₇N: C, 54.01; H, 5.46. Found: C, 54.00; H, 5.61.

2,4-Dihydroxy-3,5-dimethoxybenzoic Acid, (2,3,4,5-Tetrahydroxybenzoic Acid 3,5-Dimethyl Ether), (CH₃O)₂(HO)₂C₆H.COOH.—Five grams of methyl aminosyringate hydrochloride were dissolved in a mixture of 10 g. concentrated sulfuric acid and 50 cc. water, and the solution diazotized by the addition of 10 g. sodium nitrite dissolved in 50 cc. water. The reaction was completed by heating for two hours at 100°. As the solution was then yellow and slightly cloudy, it was coagulated by the addition of a little acetic acid, and the precipitate filtered out and dried at 104–8°. The product was soluble in alcohol or benzene and, when purified, formed pale yellow crystals, melting with decomposition at 165°. Yield, 80%. The addition of ferric chloride to its solution colors it a rich brown.

Calc. for C₈H₁₀O₆: C, 50.5; H, 4.7. Found: C, 50.61; H, 4.69.

When the nitrite solution was added directly to the aqueous solution of the amino ester hydrochloride, in absence of sulfuric acid, a rich red precipitate was formed, the nature of which has not yet been determined.

What is apparently the 2,5-dimethyl ether of 2,3,4,5-tetrahydroxybenzoic acid has been prepared by Bartolotti¹ by the fusion of apioic acid with potassium hydroxide. He describes it as a crystalline solid, melting at 147–8°.

The following preliminary experiment also was carried out: Some of the acid was heated for 40 minutes, the temperature rising finally to 220°. Gas was evolved, and the mass turned purplish. The crude product was purified by crystallization from alcohol, and the purified substance shaken with sodium hydroxide solution and dimethyl sulfate, the solution boiled for a short time, acidified, the precipitate filtered out, decolorized by boiling with boneblack in alcoholic solution, and recrystallized from the same solvent. The product was obtained in colorless, glassy needles, m. p. 89° (corr.); soluble in alcohol, ether or

¹ *Gazz. chim. ital.*, 22, I, 562 (1892).

benzene, but not appreciably soluble in water. This experiment will be repeated with larger amounts as soon as sufficient initial material is available.

An apionol dimethyl ether has been prepared by Ciamician and Silber¹ by heating apiolic acid with potassium hydroxide and absolute alcohol. They describe it as a crystalline compound, m. p. $105-6^{\circ}$, b. p. 298° ; soluble in hot water, in alcohol, ether, benzene or alkalies. The same authors,² by fusing dill oil apiolic acid with potassium hydroxide, obtained an isomeric apionol dimethyl ether as a liquid, b. p. 283° . Both of these yield, on further methylation, tetramethyl apionol, as a crystalline solid, the melting point of which is given by Ciamician and Silber as 81° , and by Boëris³ as 89° .

It will be seen that the product of our preliminary experiment, which should be the tetramethyl apionol, agrees in its melting point with that given by Boëris for this substance.

Diacetyl Derivative.—A mixture of 10 g. of the above dihydroxy acid, 30 cc. acetic anhydride and 0.5 g. fused sodium acetate, was heated to boiling for a short time; the solution was then cooled and a dilute solution of sodium acetate added. Fine, colorless crystals separated, decomposing at 162° ; soluble in alcohol, but practically insoluble in water or in dilute acids.

Subs. 0.2642: CO_2 , 0.5057; H_2O , 0.1188. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_8$: C, 52.34; H, 4.69. Found: C, 52.21; H, 5.0.

Summary of Results.

1. Methyl bromotrimethylgallate is not an oil when pure, as stated in the literature, but a colorless crystalline solid, m. p. 90° (corr.). It can be most conveniently prepared by bromination of methyl trimethylgallate in acetic anhydride solution, at low temperature.

2. The following new derivatives of syringic acid have been prepared and studied; ethyl syringate, isoamyl syringate, methyl acetylsyringate, methyl bromosyringate, methyl and ethyl nitrosyringates, methyl aminosyringate, its hydrochloride and diacetyl derivative, hydroxy syringic acid (2,4-dihydroxy-3,5-dimethoxybenzoic acid) and its diacetyl derivative.

3. The action of heat upon the hydroxy syringic acid, followed by methylation, appears to yield apionol tetramethyl ether.

4. The chief product of the action of nitric acid upon syringic acid is the hitherto unknown 3,4-dinitropyrogallol-2,6-dimethyl ether.

The work is being continued.

NEW YORK, N. Y.

¹ *Ber.*, 22, 119, 2482 (1889).

² *Ibid.*, 29, 1807 (1896).

³ *Ibid.*, 29, 1808 (1896).

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE PREPARATION OF MELIBIOSE.

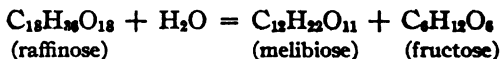
By C. S. HUDSON AND T. S. HARDING.

Received September 4, 1915.

The difficulty one meets in obtaining a supply of melibiose is doubtless the explanation of the fact that this rare disaccharide is rather seldom the subject of scientific investigation. There are two reasons why the sugar is so rare: first, the only known source for it is the trisaccharide raffinose, which itself has been somewhat rare, and, second, the methods which may be found in the literature for preparing melibiose from raffinose are not satisfactory as regards the yield, in part because the details of procedure are not specified with the exactness that is necessary to enable a reader to repeat an author's preparation of a substance which crystallizes with much difficulty. Being in need recently of a supply of melibiose, we worked out the details of its preparation from raffinose, and the procedure which we recommend, after the preparation by it without difficulty of nearly a kilogram of melibiose, will presently be described.

The Source.—As mentioned, raffinose is the only known natural source for melibiose. Recently we have described in detail an inexpensive method for the preparation of raffinose from cottonseed meal¹ which yields about 4% of the weight of the meal as pure crystalline raffinose. This quantity is approximately half the raffinose that exists in the meal. Raffinose can now be prepared with certainty and at little expense and it should no longer be considered a rare sugar. For the preparation of melibiose, it is important that the raffinose be pure; it should be colorless, of correct specific rotation, without action on Fehling's solution, and should yield less than 0.1% ash.

Methods of Bau and of Loiseau for Preparing Crystalline Melibiose.—The starting point of these methods is the fermentation of raffinose by top yeast, which proceeds as follows:



The yeast splits off fructose from raffinose and converts this hexose to carbon dioxide and alcohol, but the residual melibiose is not attacked by top yeast, though bottom yeast does ferment it. After the fermentation of the fructose is ended, Bau² decolorizes the solution with bone char, precipitates the sugar as a sirupy phase by the addition of alcohol and ether, converts the sugar to an insoluble compound with barium hydroxide, regenerates the sugar by decomposing this compound with

¹ THIS JOURNAL, 36, 2110 (1914).

² *Wochschr. Brau.*, 16, 397-400 (1899). See also *Chem. Ztg.*, 26, 69 (1902), and *Z. Ver. D. Zuckerind.*, 41, 481 (1904).

carbon dioxide or sulfuric acid and evaporates the filtrate, an aqueous solution of melibiose, to a thick sirup. Alcohol is added to saturation, followed by ether, and the solution is set aside to crystallize slowly. Bau does not record the yield. Bau has also prepared melibiose by hydrolyzing raffinose with weak acetic acid instead of with yeast, but the yield is not stated.

Loiseau¹ has prepared melibiose by a more direct method. After the fermentation of a 10–20% solution of raffinose with top yeast is completed, the liquid is heated, neutralized, filtered, and the filtrate evaporated to a sirup of about 30% water content, which very slowly crystallizes after being seeded with melibiose crystals. Loiseau also suggests concentrating the filtrate to 50% water content only, adding 95% alcohol until the solution is of about 70% alcoholic strength, seeding and setting aside at 15–20° for a slow crystallization. Loiseau does not record the yields of melibiose by these procedures, but in our opinion they could not have been large, because the sugar was crystallized from solutions which contained much water.

A Rapid Method for Preparing Pure Melibiose from Raffinose.—We have followed the main lines of Loiseau's method and in the following give in detail the description of a procedure by which we have uniformly obtained yields of 175–200 g. of melibiose from 500 g. of raffinose.

Five hundred grams of pure raffinose were dissolved to make approximately a 10% aqueous solution. It had a reading of +60° Ventzke in a 2 dcm. tube. From the specific rotations of raffinose (123°) and melibiose (143°), and the mass proportions of the reaction equation, it was calculated that the solution would have a reading of +47° Ventzke after fermentation with top yeast. About 10 g. of baker's yeast were added, together with a drop or two of glacial acetic acid, and about 1 g. of malt sprouts as a nitrogenous yeast food. Fermentation proceeded at room temperature. The optical rotation of the solution was observed at intervals. It rapidly fell to a value several degrees below +47°, which we attribute to the rapid hydrolysis of raffinose to melibiose and fructose by the enzyme invertase of the yeast. Since fructose is levorotatory its accumulation in the solution would cause a drop in dextrorotation of the kind observed. As the fermentation proceeded the rotation gradually increased and became stationary during some hours at 47.5°, a value slightly above the end point. This peculiarity seems to be due to the rapid removal of fructose by the yeast during the very active stage of fermentation, because if it is fermented about as rapidly as it is produced from the raffinose (and the enzymotic hydrolysis becomes slow when the raffinose concentration becomes small), the residual raffinose would cause the observed excess of dextrorotation. After 36–48

¹ *Z. Ver. D. Zuckerind.*, 40, 1050 (1903).

hours from the start, fermentation had ceased and the rotation was found to be within 0.2° V. (46.8°) of the calculated end point. The solution was then cleared with a slight excess of basic lead acetate, filtered through an asbestos layer in a Büchner funnel, the excess of lead in the filtrate precipitated by H_2S , a quantity (30–40 g.) of active decolorizing carbon, such as "Eponit" or "Norit," added, and the solution again filtered. The excess of H_2S was removed from the filtrate with an air current and the solution boiled under reduced pressure to a sirup of approximately 20–25% water content. Alcohol (95%) was then added just below the point of the precipitation of a sirupy phase and some crystals of melibiose were stirred in. We are much indebted to Prof. J. J. Blanksma for a supply of these crystals, because the spontaneous crystallization of melibiose is very difficult to accomplish. After standing four days at a temperature near freezing, the solution had crystallized to a solid mass. The crystals were ground in a mortar with 75% alcohol at room temperature, filtered on a Büchner funnel, washed first with 75% alcohol, then with 95%, and afterwards dried in a desiccator. The melibiose was colorless and gave a correct value for its specific rotation, considering the crystals as $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{H}_2\text{O}$. It could be recrystallized without difficulty by dissolving to a dilute solution in water, adding decolorizing carbon, filtering, boiling under reduced pressure to a thick sirup, adding EtOH (95%) to saturation, seeding and allowing to crystallize at room temperature. In several experiments the yield has ranged between 175–200 g., as mentioned.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE.]

A SECOND CRYSTALLINE *d*-FRUCTOSE PENTACETATE. (α -*d*-FRUCTOSE PENTACETATE.)

By C. S. HUDSON AND D. H. BRAUNS.

Received September 11, 1915.

Recently¹ we described the preparation and properties of a crystalline *d*-fructose pentacetate obtained by the action of acetic anhydride and sulfuric acid on *d*-fructose. We have made different attempts to convert this fructose pentacetate into the other theoretically possible isomeric form by heating with zinc chloride in acetic anhydride solution, but very little change in specific rotation was noticed and from the solution only the original substance could be recovered. On the other hand, the action of zinc chloride in acetic anhydride solution on fructose *tetracetate* caused a considerable change in specific rotation and it seemed that an isomeric fructose *tetracetate* might be obtained. However, the crystalline sub-

¹ THIS JOURNAL, 37, 1283 (1915).

stance which was separated after the rotation had become constant proved to be a *D*-fructose *pentacetate* different from the *D*-fructose *pentacetate* described before. Whereas that fructose *pentacetate* has a melting point of 108° and a negative specific rotation $[\alpha]_D^{20} = -120.9$ (in chloroform solution) the new fructose *pentacetate* has a melting point of 70° and rotates positive $[\alpha]_D^{20} = +34.75$ (in chloroform solution). This new *D*-fructose *pentacetate* shows the same stability to zinc chloride as the other fructose *pentacetate*, therefore the usual method for establishing an equilibrium between the aldose acetates fails in this case of ketose derivatives. We have also obtained the fructose *pentacetate* of m. p. 108° from fructose tetracetate by the action of sulfuric acid and acetic anhydride, showing that identical ring formation exists in both *pentacetates*, because both have now been prepared from the same tetracetate. Therefore we would name, according to the rule previously proposed,¹ *D*-fructose *pentacetate* of m. p. 70° and $[\alpha]_D^{20} = +34.75$ the alpha form and *D*-fructose *pentacetate* of m. p. 108° and $[\alpha]_D^{20} = -120.9$ the beta form. α -Fructose *pentacetate* was also obtained directly from fructose by the action of zinc chloride in acetic anhydride solution and also by the action of pyridine in acetic anhydride solution. The sirups resulting from these reactions crystallized very slowly and it is more advantageous to prepare α -fructose *pentacetate* from the fructose tetracetate, especially as we have found an easy way to prepare the tetracetate with a fairly good yield. Fructose tetracetate was made the first time by the action of acetyl bromide on fructose at about -15° .² The yield of the pure product was small (about 5%) and prevented the further investigation of the substance. Lately a better result has been obtained by the action of a solution of hydrogen bromide in acetic anhydride (a reagent first used by J. K. Dale)³ on fructose, which gave a yield of 20% of the theory, but the easiest and cheapest way found is the action of a solution of zinc chloride in acetic anhydride at 0° , stopping the reaction as soon as the fructose has dissolved. In this way a yield of 30% can be obtained.⁴

By the action of a solution of hydrogen bromide in acetic acid (a reagent first used for this kind of reaction by E. Fischer)⁵ on β -fructose *pentacetate*, a considerable change in rotation was observed, indicating that the bromotetracetyl fructose was formed. By working up the sirupy reaction product in the usual way, tetracetyl fructose was obtained, evidently as a result of the action of water on the bromoacetyl fructose. The action

¹ THIS JOURNAL, 31, 72 (1909).

² Brauns, *Verslag. K. Akad. v. Wetensch.*, Amsterdam, 1908, p. 577.

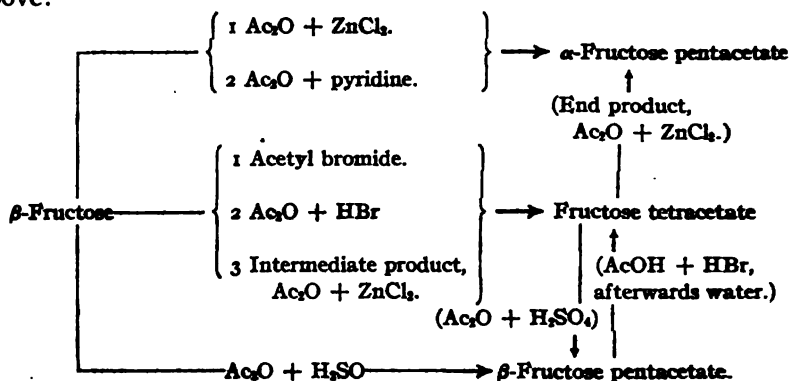
³ THIS JOURNAL, 37, 2745 (1915).

⁴ Starting with the tetracetate of fructose, we have recently prepared crystalline tetracetyl methyl fructoside. Its preparation and properties will be described in a later article.

⁵ *Ber.*, 43, 2521 (1910).

of acetyl bromide and of acetic anhydride and HBr on fructose probably also forms bromotetracetyl fructose, and this substance reacts with the water to produce fructose tetracetate. On account of the low temperature at which these reactions have to be carried on, the rotations of the solutions, which might furnish further evidence on this point, are not so easy to follow. The action of hydrogen bromide in acetic acid solution on α -fructose pentacetate did not give any change in rotatory power and the original α -fructose pentacetate was recovered.

The following scheme gives a summary of the different reactions stated above:



The pure, powdered crystalline fructose which was used for the reactions must be regarded as the β -fructose, as the initial negative specific rotation of about -140° in aqueous solution changes towards an equilibrium of about -90° . The action of zinc chloride in acetic anhydride solution on β -fructose resulted in an α -derivative and therefore we expected that an α - and β -fructose tetracetate would be the intermediate products. β -Fructose *pentacetate*, which may be formed as a by-product in this reaction, cannot be one of the intermediate products leading up to α -fructose pentacetate, because we have found, as stated above, that β -fructose pentacetate is not changed by a solution of zinc chloride in acetic anhydride. We have been unable to separate another fructose tetracetate from this reaction, though we stopped it at different stages. The formation of the known fructose tetracetate from β -fructose pentacetate by means of hydrogen bromide and acetic acid, followed by the action of water, is an indication by analogy with the aldose sugars that the described fructose tetracetate is a β -derivative. Also its high negative rotation (about -91) suggests this view.

Experimental.

Improved Methods for the Preparation of Fructose Tetracetate.—Instead of acetyl bromide, acetic anhydride saturated with HBr gas, the reagent recently recommended by J. K. Dale, was used. Thirty

grams of pure recrystallized *d*-fructose were added in the form of fine powder to 150 cc. of reagent, containing per 100 g. acetic anhydride about 51 g. hydrogen bromide, and the mixture was cooled by ice water and vigorously stirred by a motor driven glass paddle. After an hour nearly all the fructose had dissolved. The reaction product was vigorously shaken with 400–500 cc. ice water and the solution stirred for a couple of hours with cooling, in order to convert the acetic anhydride into acetic acid. The solution was neutralized in a large dish with sodium bicarbonate, separated from the excess of solid bicarbonate by filtration and the residue on the filter washed with chloroform to dissolve the adhering acetylated sugar. The filtrate was extracted with chloroform for the same purpose. The chloroform solutions were mixed, dried with calcium chloride and distilled *in vacuo* to a small volume, 30–50 cc. This solution was then spread in a thin layer on a flat crystallizing dish and a strong current of air was passed over the yellowish fluid, adding occasionally some ether. The separated crystals were filtered by suction and the mother liquor put aside for further crystallization. In this way a yield of 19–20% of fructose tetracetate was obtained. For recrystallization, fructose tetracetate was dissolved in boiling absolute alcohol and filtered. After cooling, an equal amount of ether was added. If the alcoholic solution was yellow, some eponite or other decolorizing carbon was added before filtering. The alcohol-ether solution was allowed to evaporate in a beaker in the air.

The easiest and cheapest method found for the preparation of tetracetyl fructose was the following: One hundred grams of very pure recrystallized *d*-fructose were added in the form of fine powder with stirring to a solution of 9 g. zinc chloride in 500 cc. acetic anhydride which was cooled to near 0° by an ice bath. When the reaction started a considerable amount of heat was set free and careful cooling according to need with ice was required. After half an hour's stirring of the mixture, the ice bath was taken away and the cooling continued during the next half hour with water at about +10°. Afterward the stirring was continued another half hour at room temperature and then, without further standing, the sugar having nearly completely dissolved, an equal amount of cold water was added and the stirring continued for a couple of hours with cooling in order to convert the acetic anhydride into acetic acid. The reaction product was worked up as described above, yielding about 70 g. of fructose tetracetate or 30% of the theoretical.

Methods of Preparation and Properties of α -*d*-Fructose Pentacetate.—

Forty grams of fructose tetracetate were dissolved in 600 cc. acetic anhydride and 2 g. zinc chloride in small pieces were added and dissolved by shaking. This solution of fructose tetracetate in acetic anhydride had a negative specific rotation of -85.6° , which changed after the

addition of the ZnCl_2 and 24 hours' standing at room temperature to the constant value +9.5. The solution was diluted with an equal amount of cold water and stirred for a couple of hours with cooling in order to convert the excess of acetic anhydride to acetic acid. This solution was worked up as described before and it gave a sirup which, after the addition of a small amount of absolute alcohol and occasional stirring, crystallized. The crystals were separated by suction, yielding about 36 g. of a fairly pure product. This was recrystallized by dissolving in a small amount of chloroform, filtering and evaporating the chloroform solution with a dry current of air to a thick sirup and adding a small amount of absolute alcohol. By rubbing the walls of the vessel with a glass rod crystallization was induced. A second recrystallization did not change the rotatory power and melting point. The substance α -fructose pentacetate melts at 70° . It is colorless, odorless and has a bitter taste. Its crystallizing power is much less than that of β -fructose pentacetate, though its crystalline form can be easily distinguished without a magnifying glass. It is easily soluble in the usual solvents except in water and petroleum ether.

0.2517 and 0.2850 g. gave 0.4550 and 0.5156 g. CO_2 and 0.1287 and 0.1437 g. H_2O . Calc. for $\text{C}_6\text{H}_7\text{O}(\text{C}_2\text{H}_3\text{O}_2)_5$: C, 49.21%; H, 5.68%. Found: 49.30 and 49.34% C and 5.72 and 5.64% H.

α -Fructose pentacetate was saponified in the same way as β -fructose pentacetate. By shaking 0.4000 g. powdered α -fructose pentacetate with 70 cc. 0.1 *N* sodium hydroxide during 3 hours at 0° and titrating with 0.1 *N* sulfuric acid and phenolphthalein, the amount of acetic acid produced was found to be 76.88%. In a similar experiment of 5 hours' duration the value 77.26% was found and in a third, also lasting 5 hours, the value was 77.20%. The theoretical quantity for a fructose pentacetate is 76.93%.

Evidently the saponification is complete after 3 hours. The solution was levorotatory after saponification, indicating the regeneration of fructose.

The molecular weight of α -fructose pentacetate was determined by the lowering of the freezing point of benzene. In three experiments 1.6291, 3.4506 and 4.719 g. α -fructose pentacetate per 100 g. benzene gave the respective depressions 0.212° , 0.435° and 0.575° from which the values 389, 398 and 410 are calculated for the molecular weight in comparison with the theoretical value 390.

The specific rotation of α -fructose pentacetate was measured in chloroform solution. 2.000 g. α -fructose pentacetate after one recrystallization were made up to 25 cc. with chloroform¹ and the solution polarized in a 1 dcm. tube at 20° with sodium light 2.75 circular degrees to the right, hence $[\alpha]_D^{20} = +34.4^\circ$. After a second recrystallization from chloroform-alcohol, 2.000 g. α -fructose pentacetate made up in the same manner rotated 2.78 circular degrees to the right hence $[\alpha]_D^{20} = +34.75$, which is taken as the specific rotation of the pure substance.

The mother liquor of the first recrystallization of α -fructose pentacetate

¹ *Chloroformum purificatum*, U. S. P.

from several preparations, crystallized after standing in a desiccator, yielding about 10 g. of a crystalline substance of m. p. 64–65° and a specific rotation of -7.8° . The wash fluid and mother liquor of these crystals crystallized again. The new crystalline product had a m. p. of 55–56° and a specific rotation of -19° . 0.250 g. of this substance was saponified in the usual way by shaking with 0.1 *N* sodium hydroxide for 3½ hours at 0°. Under the same conditions samples of 0.250 g. of fructose tetracetate and α -fructose pentacetate were saponified, which gave the required figures, whereas the unknown substance gave values for a pentacetate. It is probably a mixture of α - and β -fructose pentacetate, but the small amount of the sample and the nearly equal solubilities of the fructose pentacetates prevented their separation.

The reaction of a solution of zinc chloride in acetic anhydride on fructose tetracetate, which resulted in the formation of α -fructose pentacetate, was stopped at different points in order to learn if an intermediate product was formed, possibly the hypothetical α -fructose tetracetate. In one experiment the reaction was stopped when the specific rotation had reached about -30° . The only crystalline substance which could be separated in the ordinary way proved to be α -fructose pentacetate. In a second experiment the reaction was stopped before this point was reached, at a specific rotation of about -50 . Starting from 4 g. fructose tetracetate 1.25 g. of fructose tetracetate was recovered and about 0.4 g. of α -fructose pentacetate, but no other crystalline substance could be separated.

In attempts to obtain α -fructose pentacetate directly from fructose by the action of zinc chloride in acetic anhydride solution we obtained a colorless sirup, which only partially crystallized after standing a month in a vacuum desiccator with occasional seeding and stirring. Five grams zinc chloride were dissolved in 250 cc. acetic anhydride and 50 g. powdered pure fructose were added under stirring, keeping the mixture at about $+10^\circ$. When the fructose was dissolved, the reaction fluid was put aside for one night in order to convert the fructose tetracetate into α -fructose pentacetate. The following morning the specific rotation (assuming that all fructose was converted into pentacetates) was found to be $+10.0$. The fluid was worked up in the usual way, yielding a colorless sirup which slowly crystallized. From it were obtained about 8 g. of α -fructose pentacetate and a large amount of mother liquor, which did not crystallize on long standing. Therefore, α -fructose pentacetate may be prepared directly from fructose but the yield is not so good as that obtained by the acetylation of fructose tetracetate.

α -Fructose pentacetate was also obtained by using pyridine as a catalyst of the acetylation.¹ Ten grams of powdered pure fructose were added to a mixture of 67 cc. pyridine and 50 cc. acetic anhydride, which was

¹ Behrend and Roth, *Annalen*, 331, 364 (1904).

cooled to 0° and vigorously stirred by a motor driven glass paddle. After 3 hours the fructose was dissolved and the solution was kept for two days in the ice box. The solution was then poured into 250 cc. ice water, an oil separated, and the supernatant fluid was poured off. The oil was stirred several times with petroleum ether in order to extract the pyridine but the remaining sirup crystallized only after several months' standing. The crystals were separated by pressing between filter paper and amounted to about 1 g. They melted at about -62° and showed a specific rotation of $+28.1$. After one recrystallization the m. p. changed to 70° and the specific rotation to $+35.5^{\circ}$.

0.300 g. of these crystals were saponified by shaking with 70 cc. 0.1 *N* sodium hydroxide at 0° during 3 hours. By titrating with 0.1 *N* sulfuric acid and phenolphthalein the amount of acetic acid produced was found to be 76.42%. The theoretical quantity for fructose pentacetate is 76.93%.

These results show that α -fructose pentacetate is formed by the action of a solution of pyridine in acetic anhydride on fructose.

Conversion of Fructose Tetracetate into β -Fructose Pentacetate.—This reaction is important, as it establishes, in combination with the above mentioned results, that the described α - and β -fructose pentacetates have identical ring formation. Twenty grams of fructose tetracetate were added in the form of fine powder to a mixture of 120 cc. acetic anhydride and 5 cc. concentrated sulfuric acid, which was cooled by an ice and salt bath and vigorously stirred by a motor driven glass paddle. The fructose tetracetate dissolved easily. After three-quarters of an hour, 300 cc. ice water were added and stirring was continued for $1\frac{1}{2}$ hours under cooling with ice water. The mixture was neutralized in a large dish with sodium bicarbonate and further treated as has been described for the preparation of fructose tetracetate. The yield was 17 g. crystals melting gradually from $99-105^{\circ}$ and showing a specific rotation of -106.3 . The crystals were washed with ether and the specific rotation rose to -114.4° . After one recrystallization the specific rotation increased to -118.6° and a second recrystallization from ether brought it to -120.5° , a value which was changed only slightly by a further recrystallization. The specific rotation was therefore found to agree with β -fructose pentacetate (-120.9°) and also the melting point of the recrystallized product, $108-109^{\circ}$, was found to be identical with that of the β -pentacetate. The presence of small amounts of unaltered fructose tetracetate is probably the reason that the pure β -fructose pentacetate cannot be obtained as readily by this reaction as by its preparation from fructose, which has been previously described.¹

Experiments for Establishing an Equilibrium between the Fructose Pentacetates and for Converting Fructose Tetracetate to an Isomeric Form.—As has been stated in the introduction, no equilibrium could be

¹ THIS JOURNAL, 37, 1283 (1915).

established between the fructose pentacetates by the usual method of heating with ZnCl_2 in acetic anhydride solution, and therefore it is concluded that the ketose pentacetates differ in this respect from the aldose pentacetates. Three grams of β -fructose pentacetate were dissolved in 25 cc. acetic anhydride. The specific rotation was found to be -121.8° and it was not changed by heating the solution for $\frac{1}{4}$ hour on the steam bath. After dissolving 0.3 g. zinc chloride the specific rotation changed to -111.2° . After keeping this solution for 2 days at room temperature the specific rotation was -107.4° and the color yellow. The solution was heated for 10 minutes on the steam bath and the rotation changed to -103.6° . This rotation did not change further in two subsequent reheatings. The fluid was worked up in the ordinary way and yielded about 1 g. of β -fructose pentacetate, which was identified by the specific rotation.

The next experiment was made with α -fructose pentacetate. Three grams α -fructose pentacetate were dissolved in 25 cc. acetic anhydride and the specific rotation was found to be $+26.5^\circ$. After dissolving 0.3 g. zinc chloride the specific rotation changed to $+26.1^\circ$ and remained the same after heating for 10 minutes on the steam bath. A subsequent heating of 30 minutes on the steam bath changed the specific rotation to $+26.8^\circ$ and turned the solution slightly yellow. From this solution nearly the original amount of α -fructose pentacetate was recovered, which was identified by the melting point and specific rotation. Therefore zinc chloride does not change α -fructose pentacetate. The action of sulfuric acid on solutions of α - and β -fructose pentacetates in acetic anhydride also did not establish an equilibrium between the fructose pentacetates. The solutions gradually became dark brown and no other substance than the respective pentacetate could be recovered from them. Boiling with acetic anhydride (b. p. 138°) also did not change α - and β -fructose pentacetate. After $\frac{1}{4}$ hour boiling the specific rotation of β -fructose pentacetate in acetic anhydride remained the same, $+26.1^\circ$, and the specific rotation of β -fructose pentacetate changed only from -121.6° to -118.4° . After a subsequent boiling of $\frac{1}{4}$ hour the specific rotations were, respectively, $+25.4^\circ$ and -117.1° . From both solutions nearly all the original substance was recovered.

The tetracetate of fructose shows similar behavior and has not changed in solution to an isomer. Whereas tetracetyl glucose shows mutarotation in alcoholic solution¹ tetracetyl fructose does not show any change in rotation in absolute or 50% alcohol. The addition of a few drops glacial acetic acid did not produce any change. Also a 50% alcoholic solution made up and polarized at $3-4^\circ$ did not show a change in rotation more than 0.1° , when the solution was gradually changing to a temperature

¹ E. Fischer, *Ber.*, 42, 2778 (1909).

of 20° . Further, the action of zinc chloride in glacial acetic acid solution did not materially change the specific rotation. Two grams fructose tetracetate were dissolved in 25 cc. glacial acetic acid. The specific rotation was found to be -80.0° . After dissolving about 50 mg. ZnCl_2 the specific rotation was -79.5° and after $1/4$ hour heating on the steam bath -79.8° . After dissolving 2 g. zinc chloride on the steam bath in 5 minutes the specific rotation was -78.0° . When small amounts of sulfuric acid or ammonia are added to an acetic anhydride solution of fructose tetracetate a material change in rotation goes hand in hand with a saponification and destruction.

Action of Hydrogen Bromide in Acetic Acid Solution on α - and β -Fructose Pentacetate.—This reagent was first used by E. Fischer¹ for preparing in the most convenient way the bromoacetyl derivatives from the acetates of the aldoses. The following experiments show that the bromotetracetyl fructose is undoubtedly formed by similar action, but it could not be separated on account of its easy decomposition by water.

Seven grams of β -fructose pentacetate were dissolved in a 25 cc. measuring flask in 8 cc. glacial acetic acid and the volume completed with a saturated solution of hydrogen bromide in glacial acetic acid. The rotation was followed during 20 minutes after the addition of the hydrogen bromide reagent. The specific rotations are figured on the basis of 7 g. substance present in 25 cc. solution. The small difference in molecular weight of fructose pentacetate (390) and the bromotetracetyl fructose (411) may allow this assumption. The specific rotation of β -fructose pentacetate in acetic acid solution is -121.7 . After the mixture had stood 20, 30, 45, 65 and 85 minutes the specific rotation had the respective values, $+45.7$, $+53.6$, $+59.2$, $+60.5$, $+60.0$, which shows that in only 65 minutes the change in specific rotation amounted to more than $+180$.² By shaking this reaction product with 200 cc. ice water and working up the mixture in the described way 3.5 g. of tetracetyl fructose were obtained. Further experiments will be made to separate the bromoacetyl fructose in a crystalline state. The action of this reagent on α -fructose pentacetate was also investigated. Seven grams α -fructose pentacetate were dissolved in a 25 cc. measuring flask in 8 cc. glacial acetic acid and the volume completed with a saturated solution of hydrogen bromide in glacial acetic acid. The specific rotation of α -fructose pentacetate in glacial acetic

¹ *Ber.*, 43, 2521 (1910).

² The difference between the specific rotations of β -glucose pentacetate and bromotetracetyl glucose is $+194$, the difference for the analogous compounds of galactose $+211$, for cellose the difference is about $+110$, and for milk sugar $+110$, showing the great difference in specific rotations between the fully acetylated β -derivatives of the sugars and the bromoacetyl derivatives.

acid is +26.5. Twenty minutes after the reagent had been added the specific rotation was found to be +26.6, a value which did not change during the next thirty minutes. The solution was heated on the steam bath for 5 minutes, the color turning from yellow to a dark yellow. The specific rotation was now found to be +23.9. The solution was shaken with 200 cc. ice water and further worked up in the usual way and yielded 3 grams of a crystalline substance melting at 70° with a specific rotation in chloroform solution of +34.3. Therefore about half of the original α -fructose pentacetate has been recovered, the rest probably being saponified and destroyed.

WASHINGTON, D. C.

BROMOACETYLXYLOSE AND BETA-TRIACETYLMETHYLXYLOSIDE.

By J. K. DALY.¹

Received September 11, 1915.

During an investigation of methods for brominating and acetylating the sugars, there was obtained from xylose a crystalline bromoacetyl derivative which is very similar in properties to the acetohalogen derivatives of other sugars. The bromine atom is very active and can be readily replaced by an oxyacetyl group, forming tetracetyl xylose, or by an oxymethyl group forming a triacetylmethylxyloside. This latter compound, on hydrolysis with dilute alkali, yields the well-known β -methylxyloside. This correlation, together with its analysis, low rotation and method of preparation, appears sufficient to justify the naming of this acetylated methyl xyloside, β -triacetylmethylxyloside.

Preparation of Bromoacetylxylose.—Emil Fischer² has prepared the bromoacetyl derivative of several of the sugars by the action of a saturated solution of hydrobromic acid gas in acetic acid on the corresponding completely acetylated sugar. The action of acetyl bromide directly upon the sugars has also been employed by a number of investigators for the preparation of these compounds. Bodart³ successfully prepared chloroacetyl lactose by suspending lactose in acetic anhydride and passing gaseous hydrochloric acid into the mixture. From consideration of these results, it appeared probable that a concentrated solution of hydrobromic acid in acetic anhydride would act directly upon the sugars, giving the bromoacetyl derivatives. The following method for the preparation of bromoacetyl xylose has also been employed successfully in the preparation of bromoacetyl lactose, bromoacetyl maltose, and

¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² *Ber.*, 43, 2530 (1901); 44, 2537 (1902).

³ *Monatsh.*, 23, 1 (1902).

bromoacetyl glucose, with yields of from 55–70% of the theoretical amount. Mannose and galactose have not given, by this method, crystalline compounds.

Twenty-five grams of finely ground xylose were treated in an Erlenmeyer flask at room temperature with 150 cc. of a saturated solution of hydrobromic acid in acetic anhydride. A very violent reaction followed. The resulting straw-colored sirup was cooled, mixed with 300 cc. of chloroform and the solution shaken with ice-water, sodium bicarbonate solution, and again three or four times with water. After drying with calcium chloride the chloroform solution was evaporated at 50° under diminished pressure to a thick sirup. This was dissolved in a little dry ether and on rapid evaporation beautiful crystals formed spontaneously. The substance thus obtained was evidently somewhat impure, because it decomposed in the air in a very short time with the evolution of hydrobromic acid fumes. On purification by recrystallization from dry ether the compound became more stable and could be kept for several hours without appreciable signs of decomposition.

For analysis 0.4405 g. of the pure, dry substance was dissolved in methyl alcohol, a drop of strong nitric acid added and the bromine precipitated as silver bromide by an aqueous solution of silver nitrate.

Obtained, 0.2407 g. silver bromide, corresponding to 23.25% bromine.

Calc. for $C_8H_{10}O_4(C_2H_5O)_3Br$: bromine, 23.57%. Found, 23.25.

Triacetyl bromoxylose is very soluble in chloroform, benzene and acetone, rather soluble in ether and almost insoluble in ligroin. It was recrystallized from dry ether until its specific rotation became constant. The melting point of the pure substance dried in a vacuum desiccator was 102° (uncorr.). In chloroform¹ solution, 0.6360 g. of the compound per 25 cc. of the solution gave a reading to the right, +10.8°, in a two decimeter tube, using sodium light, hence $[\alpha]_{20}^D = +212.2^\circ$. A duplicate measurement, in which 0.7930 g. of the compound were used, gave $[\alpha]_{20}^D = +212.1^\circ$. The identification of this compound was confirmed by converting it into β -tetracetylxylose and into β -triacetylmethylxyloside, using the methods by which Koenigs and Knorr² prepared β -pentacetyl glucose and β -tetracetylmethylglucoside from bromoacetyl glucose.

Preparation of β -Triacetylmethylxyloside.—For the preparation of this compound, it is not necessary to have the bromoacetylxylose in a very pure condition. If the sirup obtained by evaporating the chloroform extract is stirred well with petroleum ether, it soon hardens to a semicrystalline mass, which can be used without further purification. This product is dissolved in ten times its weight of methyl alcohol and

¹ *Chloroformum Purificatum*, U. S. P., was used throughout this work.

² *Ber.*, 34, 970 (1901).

solution of silver nitrate in 80% methyl alcohol is added until complete precipitation of the silver bromide is effected. The filtrate from the silver bromide is treated with hydrogen sulfide and shaken with barium carbonate. The filtrate from this is evaporated to a thick sirup on the steam bath under diminished pressure. This sirup is dissolved in a little hot water which, on cooling, deposits thin plate-like crystals, which analysis and conversion into β -methylxyloside show to be β -triacetylmethylxyloside. The crystalline substance is very soluble in chloroform, alcohol, ether and hot water. It was purified by recrystallization from water until its specific rotation became constant. The melting point of the pure substance dried in a vacuum desiccator over calcium chloride was 115° (uncorr.). With chloroform as solvent, 0.5785 g. of this compound per 25 cc. of the solution gave a reading to the left, -2.8° in a two decimeter tube, with sodium light, hence $[\alpha]_{20}^D = -60.5^{\circ}$. After another recrystallization, a duplicate measure, in which 0.6751 g. of the compound was used, gave $[\alpha]_{20}^D = -60.8^{\circ}$.

0.2274 g. and 0.2078 g. gave 0.4149 and 0.3800 g. CO_2 and 0.1272 and 0.1163 g. H_2O , corresponding to 49.76 and 49.87% C and 6.26 and 6.26% H.

Calc. for $(\text{C}_6\text{H}_6\text{O}_4)(\text{CH}_3\text{O})(\text{C}_2\text{H}_3\text{O})_3$: 49.63% C and 6.25% H.

Two acetyl determinations, made by shaking 0.25 g. of the substance with 70 cc. 0.1 N NaOH for two hours in a glass-stoppered bottle at 0° , gave 61.94 and 62.27% acetic acid, which agree with the theoretical value for triacetylmethylxyloside, 62.07%.

Conversion of β -Triacetylmethylxyloside into β -Methylxyloside.—0.4575 g. of the first-named compound was shaken with about 50 cc. 0.1 N NaOH for two hours. The solution was then neutralized with H_2SO_4 and evaporated to dryness. The residue was extracted with hot ethyl acetate which on evaporation deposited crystals that melted at 155 – 156° and had a specific rotation $[\alpha]_{20}^D = -65.3^{\circ}$. Obtained 0.13 g. Fischer¹ gives for β -methylxyloside, m. p. 156 – 157° and $[\alpha]_{20}^D = -65.8^{\circ}$.

Conversion of Bromoacetylxylose into β -Tetracetylxylose.—Four grams of crude bromoacetylxylose were dissolved in 75 cc. of galcial acetic acid. This solution was shaken a few minutes with 5 g. of silver acetate. The filtrate from the silver bromide precipitate was neutralized with sodium bicarbonate and extracted with chloroform. This extract was concentrated to a thick sirup under diminished pressure and the sirup dissolved in a little ether. Crystals soon appeared of m. p. 126 – 127° (corr.) and $[\alpha]_{20}^D = -24.9^{\circ}$ in chloroform solution.

Hudson and Johnson² found for β -tetracetylxylose $[\alpha]_{20}^D = -25.1^{\circ}$ (chloroform solution) and m. p. 128° (corr.).

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¹ Ber., 28, 1158 (1895).

² Following article by Hudson and Johnson.

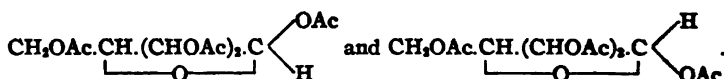
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE ISOMERIC TETRACETATES OF XYLOSE, AND OBSERVATIONS REGARDING THE ACETATES OF MELIBIOSE, TREHALOSE AND SUCROSE.

By C. S. HUDSON AND J. M. JOHNSON.

Received September 11, 1915.

Crystalline xylose tetracetate has been prepared by Stone¹ through the action of acetic anhydride and sodium acetate upon the sugar, and he records its melting point as 123.5–4.5° and its specific rotation in absolute alcohol –25.43°. Bader² has found the substance to melt slightly higher, 126°. We have recently converted this tetracetate to an isomeric form by heating it in acetic anhydride solution with a trace of zinc chloride, as will presently be described. The new tetracetate and the one prepared by Stone represent a pair of isomers similar to the alpha and beta forms of the pentacetates of mannose and glucose and the octacetates of cellulose, maltose and lactose, and their structures may accordingly be written, assuming a gamma lactonyl ring,



Since the specific rotations of the two tetracetates in chloroform solution (*vide infra*) are, respectively, –25° for Stone's form and +49° for the new isomer, it is highly probable that the latter is a derivative of the strongly dextrorotatory alpha form of xylose, and the former a derivative of the hypothetical beta xylose,³ and in conformity with this view we will designate the new tetracetate as the alpha form and Stone's tetracetate as the beta modification. We have sought to complete the evidence on this point by correlating one of these tetracetates directly with crystalline alpha xylose by acetylating this sugar with acetic anhydride and pyridine at 0°, but the reaction has yielded both tetracetates, due doubtless to a partial transformation of alpha xylose to its beta form in advance of the acetylation.

Rearrangement of β -Xylose Tetracetate to the Isomeric Alpha Form.—

A considerable quantity of the β -tetracetate was prepared according to Stone's directions, using the proportions one part fused sodium acetate, four parts pure xylose, and sixteen parts acetic anhydride, and pouring the reaction mixture into water as soon as the xylose had dissolved. After recrystallizing the tetracetate from water and from 95% alcohol until its rotatory power reached a constant value, the m. p. of the pure sub-

¹ *Am. Chem. J.*, 15, 653 (1893).

² *Chem. Ztg.*, 19, 55 (1895).

³ *THIS JOURNAL*, 31, 76 (1909).

stance was found to be 128° (corr.). Its specific rotations in several solvents are recorded in Table I. The yield of pure β -tetracetate was 22 grams from 25 grams of xylose. When this tetracetate was dissolved in acetic anhydride containing a small amount of zinc chloride and the solution was heated on the steam bath, a change in specific rotation from -23.3° to the constant final value $+71.8^{\circ}$ was observed, only four minutes, or less, being required for the completion of the mutarotation. The product was poured into cold water and a partial crystallization of the insoluble sirupy layer soon took place. The mass was thinned with alcohol and the crystals removed. They proved to be the original β -tetracetate. The sirupy alcoholic mother liquor, on cooling with ice, gave fine, flaky crystals which could be filtered while cold, though they melted somewhat below room temperature. They appear to be an unstable alcoholate of α -xylose tetracetate, but a trustworthy analysis of them could not be obtained on account of the fact that they readily change to crystals of α -tetracetate, without alcohol, on recrystallization. Estimations of the alcoholic content of the crystals by direct evaporation and also by specific-gravity measurements of their distillate on boiling with water, showed percentages varying from 12 to 33, indicating that the crystals were mixtures of alcoholate and alcohol-free tetracetate. When the crystals of the alcoholate were dissolved in a little alcohol at room temperature, there crystallized spontaneously the new α -xylose tetracetate. In another case, a batch of crystals of the alcoholate was found to change entirely to crystals of the new tetracetate, free of alcohol, on standing several days in alcohol near 0° . The α -tetracetate was recrystallized from alcohol until its specific rotation reached the constant values that are recorded in Table I. The substance melts at 59° (corr.). The yield is about 50% of the weight of the β -tetracetate. For analysis the compound was dried in a vacuum desiccator over KOH.

0.2584 and 0.2675 g. substance yielded 0.4640 and 0.4806 g. CO_2 , and 0.1341 and 0.1378 g. H_2O .

Calc. for CHO : 49.03% C and 5.70% H. Found: 48.97 and 49.00% C, 5.81 and 5.76% H.

An acetyl estimation was made by boiling in a quartz flask with reflux quartz condenser 0.5 g. substance with 100 cc. 0.25 *N* sulfuric acid during three hours.

Calc. for xylose tetracetate: 54.09%. Found: 54.00 and 53.89% (CH_3CO).

Mol. wt. from the lowering of the freezing point in benzene. Six experiments (with 0.746 and 1.754 g. per 100 g. solvent) showed depressions varying between 0.123° and 0.267° , which indicated values for the molecular weight ranging between 303 and 329. Theoretical value, 318.

By saponifying the new xylose tetracetate with 5% alcoholic potash at 0° , xylose was regenerated, crystallized and identified. The specific rotation in water of the xylose two minutes after solution at 20° , was $+86.1^{\circ}$ and the constant rotation was $+19.4^{\circ}$.

The Rotatory Powers of the Isomeric Xylose Tetracetates.—Table I records the specific rotatory power of the new α -tetracetate in several solvents¹ in comparison with the rotation of the β -tetracetate. The tube length in all cases was 4 dcm., the specific rotations are expressed in circular degrees for sodium light, and the concentration in grams per 100 cc. of solution, the weighings being made in air with brass weights.

TABLE I.
The Specific Rotations of the Isomeric Xylose Tetracetates.

Tetracetate.	Chloroform.		Benzene.		99.5% Acetic acid	
	Conc.	$[\alpha]_D^{20}$	Conc.	$[\alpha]_D^{20}$	Conc.	$[\alpha]_D^{20}$
Alpha.....	5.02	+89.3	5.03	+79.3	3.33	+95.3
Alpha.....	9.99	+88.9	10.01	+80.4	10.04	+95.3
Beta.....	4.99	-24.7	10.03	-22.3	10.04	-7.3
Beta.....	11.07	-25.1
Difference of the Molecular Rotations of the Alpha and Beta Forms.						
Glucose pentacetate.....	38,100		36,700		40,800	
Xylose tetracetate.....	36,300		32,500		32,700	

A comparison of the differences of the molecular rotations of the α - and β -xylose tetracetates with those of the α - and β -glucose pentacetates¹ is shown in the second part of Table I, where the averaged values of Table I are multiplied by 318, the molecular weight of xylose tetracetate.

It was expected from theoretical considerations³ that these differences would be the same for the two pairs of acetylated sugars. In benzene and in acetic acid solutions, the conclusion does not hold at all well, as has been noticed previously in similar comparisons.⁴ The values are fairly close in chloroform solution, the discrepancy amounting to about six degrees in specific rotation.

Preparation of Both α - and β -Xylose Tetracetates by Acetylating α -Xylose at 0° in Pyridine Solution.—Pure crystalline α -xylose (20 g.) was acetylated at 0° with a mixture of acetic anhydride (100 cc.) and commercial pyridine bases (100 cc.) according to the directions of Behrend.⁵ After the sugar had dissolved, which required about 26 hours with occasional stirring, the mixture was kept at 0° 24 hours longer, but no change in its rotation after dissolving ($[\alpha]_D = +33$ approximately) was apparent. It was then poured into a large excess of water and the resulting insoluble sirupy layer partially crystallized. This was thinned with alcohol, and the crystals removed, which proved to be the β -tetracetate. By cooling the sirupy mother liquor with ice, crystallization of the alcoholate of α -xylose tetracetate, which has been described above, could be ob-

¹ The chloroform used was *Chloroformum purificatum*, U. S. P.

² Hudson and Dale, *THIS JOURNAL*, 37, 1264 (1915).

³ *THIS JOURNAL*, 31, 66 (1909); 37, 1266, 1275, 1279 (1915).

⁴ Hudson and Dale, *THIS JOURNAL*, 37, 1266 (1915).

⁵ *Ann.*, 331, 369 (1904); 353, 109 (1907).

tained. From these crystals the alcohol-free α -form was prepared according to the directions already recorded. The yield of α -tetracetate by this method is about 9 g.

Conversion of Acetochloroxylose to the β -Tetracetate.—Ryan and Ebrill¹ have prepared a tetracetate of xylose by the interaction of acetochloroxylose and silver acetate in glacial acetic acid. They call attention to the fact that the resulting tetracetate melted at 119° , which is considerably lower than the melting point found by Stone. It might be considered, therefore, that their tetracetate is an isomeric form of Stone's compound. However, they had in hand such a small quantity of their tetracetate, less than one gram, that we doubt whether it was possible to purify it sufficiently to decide this point. It is evident that the substance could not have been the new α -tetracetate of m. p. 59° . In repeating Ryan and Ebrill's preparation, we were not successful in obtaining crystalline acetochloroxylose by their method of treating xylose with acetyl chloride at 0° , but by boiling the sugar with this reagent and a trace of ZnCl_2 until solution was complete, acetochloroxylose was prepared in beautiful crystals, with a yield of 7.8 g. from 10 g. of xylose. It melted at $95\text{--}97^\circ$ uncorr. (Ryan and Ebrill found 101°); and its specific rotation in chloroform was to the right, $[\alpha]_D^{20} = +165^\circ$, at a concentration of 12 g. per 100 cc. A qualitative test for chlorine showed its presence. For the preparation of Ryan and Ebrill's tetracetate, 5 g. of acetochloroxylose were dissolved in 125 cc. glacial acetic acid and shaken with 4 g. silver acetate until the supernatant liquid gave no reaction for chlorine. On treating the product according to these authors' directions, we obtained 3 g. of xylose tetracetate which showed after repeated recrystallization a melting point of 125° (uncorr.) and a specific rotation in chloroform of -25° . The substance is indeed Stone's β -xylose tetracetate.

Conversion of the α - and β -Tetracetates to Acetobromoxylose and Its Conversion to the β -Triacetyl Methyl Xyloside.—Five grams of β -xylose tetracetate of specific rotation -25° were dissolved in 6 cc. glacial acetic acid, 17 cc. acetic acid saturated with hydrobromic acid gas were added, and the solution was kept at room temperature to observe any change in its polariscopic reading, but the reaction was so rapid that the reading had become constant within the first two minutes. The solution was poured into chloroform and the mixture was washed successively with ice-water, iced sodium bicarbonate solution, and ice-water again, and was then dried with CaCl_2 , and evaporated *in vacuo*. The sirup was crystallized from ether and petroleum ether and 4.3 g. acetobromoxylose were obtained, of m. p. $100\text{--}101^\circ$ (uncorr.), and specific rotation in chloroform $+210.8^\circ$. These data agree with those found by Dale (see preceding article) for acetobromoxylose, which he recently prepared. This aceto-

¹ *Proc. Roy. Dublin Soc.*, 11, 249 (1905-8).

bromoxylose was dissolved in methyl alcohol and by treatment with silver nitrate, β -triacetyl methyl xyloside¹ was obtained, of m. p. 115° (uncorr.) and $[\alpha]_D^{20} = -59.5^\circ$ in chloroform solution.

Five grams of α -xylose tetracetate of specific rotation $+89^\circ$ were brominated as described for the other tetracetate, and there were obtained 4.1 g. of acetobromoxylose, of m. p. 94–96° (uncorr.), and specific rotation in chloroform $+207.2^\circ$. This acetobromoxylose was converted as above into β -triacetyl methyl xyloside of m. p. 114–115° (uncorr.), and $[\alpha]_D^{20} = -59.3^\circ$ in chloroform solution. Therefore, the same acetobromoxylose and the same β -triacetyl methyl xyloside were obtained from the α - and β -modifications of xylose tetracetate.

Observations Regarding Melibiose Octacetate.—A supply of β -melibiose octacetate was prepared by acetylating melibiose with acetic anhydride and anhydrous sodium acetate, and the substance was recrystallized until no further change in its rotation was observed. It was found to have a m. p. of 177.5° (corr.) and specific rotations in chloroform of $+102.5^\circ$ and in 99.5% acetic acid of $+101.9^\circ$. Scheibler and Mittelmeier² found a m. p. of 170–171° and $[\alpha]_D$ in chloroform of $+9.42^\circ$, and Bau³ found in chloroform $[\alpha]_D = +98.1^\circ$. 2.8 g. of this octacetate were dissolved in acetic anhydride containing a little zinc chloride and the mixture was heated on the steam bath during 35 minutes. The specific rotation was thereby changed from $+107.0^\circ$ to $+147.3^\circ$, and longer heating caused no further increase. The solution was poured into water and after standing some days the insoluble sirupy mass was taken up in alcohol to a thick sirup. After some weeks' standing, small crystals appeared, but now after several months, we have not been able to crystallize the entire mass, and have not obtained enough crystals to make any measurements. However, on account of the large change in rotation we are of the opinion that the known octacetate of melibiose is the beta form and that the amorphous material consists largely of α -melibiose octacetate.

Observations on Trehalose Octacetate.—Trehalose octacetate was prepared according to the usual method of acetylation with acetic anhydride and anhydrous sodium acetate, a 60% yield being obtained. After recrystallization from alcohol several times, the compound melted at 96–98° (uncorr.). The same substance was obtained with a yield of 72% by acetylating the sugar with acetic anhydride and zinc chloride. Maquenne⁴ found a melting point of 97–98° for this octacetate. We have measured the rotatory power of trehalose acetate, which does not seem

¹ This compound, and its method of preparation, are described in the preceding article by Dale.

² *Ber.*, 23, 1438 (1890).

³ *Zeitschr. d. Ver.*, 1904, II, 507.

⁴ *Compt. rend.*, 112, 947 (1891).

to have been previously recorded. 5.15 g. substance made up to 50 cc. with chloroform, in a 2 dcm. tube at 20°, rotated 96.5° V. to the right, therefore, $[\alpha]_D^{20} = +162.3^\circ$. When this octacetate was dissolved in acetic anhydride with a small amount of zinc chloride, no change in its specific rotation of +147.4° could be detected after heating the solution to 100° repeatedly. Evidently there is only one trehalose octacetate.

Observations on Sucrose Octacetate.—Sucrose octacetate was prepared by the acetylation of sugar with acetic anhydride and pyridine bases, and also with acetic anhydride and sodium acetate. After recrystallization, it melted at 69° (uncorr.) and in chloroform $[\alpha]_D^{20} = +59.6^\circ$. Herzfeld¹ has found the m. p. 67°. In this case again it was not possible to obtain any evidence of the existence of an isomeric sucrose octacetate, since the specific rotation of its solution in acetic anhydride containing a trace of ZnCl₂ did not change on heating. These results with the octacetates of trehalose and sucrose are not unexpected since the parent disaccharides are not reducing sugars, do not combine with phenylhydrazine, do not exhibit mutarotation, nor occur in alpha and beta forms, and consequently do not have the type of structure which accounts for the existence of alpha and beta modifications of the aldoses and ketoses and their derivatives.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURG.]

THE CONDENSATION OF ALDEHYDE DIACETATES AND OF PHENYLHYDRAZONES WITH 2-THIOHYDANTOIN.

By BEN H. NICOLET.

Received October 14, 1915.

Five years ago, Wheeler and Hoffman² made the discovery that aromatic aldehydes can be condensed with hydantoin by boiling with glacial acetic acid and fused sodium acetate, giving compounds of Type I. Wheeler and Brautlecht³ applied the reaction to substituted 2-thiohydantoins, and Wheeler, Nicolet and Johnson⁴ showed that it worked equally well with 2-thiohydantoin itself.

These condensation products are readily reduced to benzyl (II), or substituted benzyl hydantoins,⁵ and these in turn are readily hydrolyzed to phenylalanine (III), or substituted phenylalanines. In most cases this method for preparing substituted phenylalanines compares favora-

¹ *Ber.*, 13, 267 (1880); *Z. Ver. D. Zuckerind.*, 1887, 422.

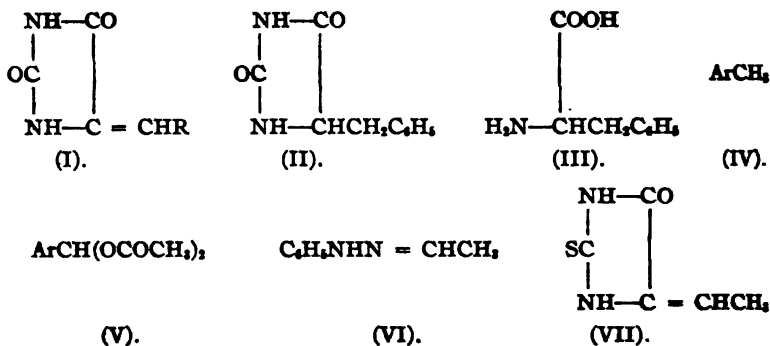
² H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, 45, 368.

³ H. L. Wheeler and C. A. Brautlecht, *Loc. cit.*, 446.

⁴ H. L. Wheeler, B. H. Nicolet and T. B. Johnson, *Loc. cit.*, 46, 456.

⁵ Wheeler and Hoffman, *Loc. cit.*; T. B. Johnson and C. A. Brautlecht, *THIS JOURNAL*, 33, 1531 (1911).

bly with that of the younger Erlenmeyer.¹ Johnson and his various co-workers have made use of it for the preparation of a number of phenylalanine and tyrosine derivatives.



During the last few years, considerable interest has been shown in the preparation of nucleus-substituted phenylalanines not hitherto found to occur as protein constituents, for use in the study of the chemistry of metabolism. As some of the acids desired are bound to require for their preparation aldehydes which cannot readily be bought, nor easily prepared in the pure state, a method was desirable which would obviate the necessity of isolating the aldehydes before condensation with hydantoins. This seems now to have been found in the use of either the α -diacetates or the phenylhydrazones, instead of the free aldehydes.

One of the simplest methods for the laboratory preparation of many aromatic aldehydes, is the oxidation of the corresponding methyl derivatives (IV) with chromic anhydride in acetic acid and acetic anhydride solution. This reaction yields the aldehyde diacetates (V). Ordinarily these are readily hydrolyzed to the aldehydes, but occasionally they are so difficultly soluble in water that the hydrolysis is unsatisfactory. In any case, the subsequent distillation with steam, and purification by means of the bisulfite, are operations that would willingly be avoided. Benzal diacetate reacts normally with 2-thiohydantoin, and there is no apparent reason why this reaction should not be a general one.

Where the regeneration of the aldehyde is not required, the phenylhydrazone is one of the favorite derivatives for its isolation and purification. It may often be found preferable to substitute phenylhydrazones for the free aldehydes when the latter are not themselves readily isolated. Benzal phenylhydrazone condenses normally with 2-thiohydantoin, and the reaction is evidently a very general one, since even phenyl glucosazone can be so condensed.

Strictly aliphatic aldehydes have not hitherto been condensed with

¹ E. Erlenmeyer, Jr., *Ber.*, 30, 2981 (1897); *Ann.*, 307, 146 (1899).

hydantoin derivatives. The higher aldehydes would be expected to react normally, but the lower members of the series are too volatile to stand heating to the required temperatures, except in a sealed tube. Here the phenylhydrazone seems to solve the difficulty, for ethylidenephnylhydrazine (VI) condenses with 2-thiohydantoin to give 2-thio-4-ethylidenehydantoin (VII), the first compound¹ of Type I, in which R is an alkyl group.

Experimental Part.

Condensation of Benzal Diacetate with 2-Thiohydantoin.—The condensation was made in the usual manner. One and seven-tenths grams of 2-thiohydantoin,² 3.5 g. (calc. 3.05 g.) benzal diacetate, and 5 g. fused sodium acetate, were added to 20 g. glacial acetic acid, and the mixture boiled for two hours under a reflux condenser in a metal bath. On diluting with water, 2-thio-4-benzal hydantoin separated, and was freed from any diacetate that might possibly be present by dissolving in dilute alkali and reprecipitating. It melted at 258°, and was identical with the product obtained by Wheeler, Nicolet, and Johnson.³ The yield was 1.9 g. of the pure product, or 61.3%.

Condensation of Benzal Phenylhydrazone with 2-Thiohydantoin.—One and two-tenths grams of 2-thiohydantoin was condensed as described above with 2.5 g. (calc. 2.0 g.) benzal phenylhydrazone. Addition of water precipitated a mixture of 2-thio-4-benzal hydantoin and unaltered phenylhydrazone, from which dilute alkali dissolved only the former. On acidifying, 1.13 g. benzal thiohydantoin was obtained, corresponding to a yield of 54%.

Both of these yields will undoubtedly be somewhat improved by working with larger quantities.

2-Thio-4-ethylidenehydantoin, VII.—Three grams of 2-thiohydantoin were condensed with a slight excess of acetaldehyde phenylhydrazone by boiling for two hours with sodium acetate in acetic acid. Addition of water precipitated the crude compound, which was purified by solution in alkali and crystallization from alcohol, in which it is readily soluble hot, and moderately soluble cold. It forms a yellow-brown crystalline powder which melts rather indefinitely at 253°, and is only very slightly

¹ Since this paper was written, Dr. Treat B. Johnson has called the writer's attention to a paper by Pinner and Lifschutz (*Ber.*, 20, 2350 (1887)), in which a compound said to be 4-ethylidenehydantoin was described. It was prepared by the fusion of α -chlorocrotonylurea, and named "ethylidene metapyrazolone." The few properties of this substance there described have caused both Dr. Johnson and myself to question whether the substance in question might not have been 4-methyluracil. This point, and also some anomalies that have been noted in the condensation of ethylidenephnylhydrazine with 3-benzoyl-2-thiohydantoin, will be further investigated.

² THIS JOURNAL, 33, 1978 (1911).

³ *Am. Chem. J.*, 46, 470 (1911).

soluble in water. The analysis shows it to be 2-thio-4-ethylidene hydantoin. Nitrogen (Kjeldahl).

Calc. for $C_4H_6ON_2S$: N = 19.72%. Found: N = 19.57%.

PITTSBURGH, PA.

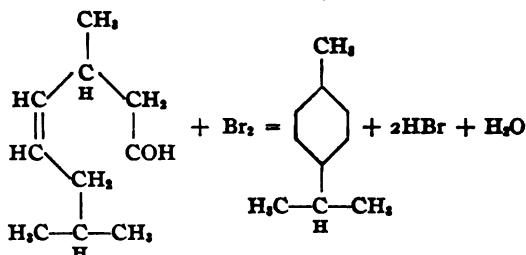
[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT CO.]

ISOPULEGOL PHOSPHONIC ACID.

By FRANCIS D. DODGE.

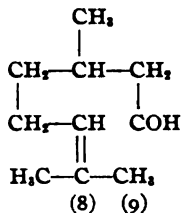
Received September 13, 1915.

The characteristic constituent of the essential oil of citronella is an aldehyde, having the composition $C_{10}H_{18}O$, and known as citronellaldehyde, or citronellal. In an investigation of this oil, in 1889,¹ the writer found that this aldehyde was an aliphatic or open-chain compound, singly unsaturated, and hence homologous with acrolein. This was one of the first examples of open-chain compounds closely related to the terpene series, and the first clue to its structure was afforded by the conversion into *p*-cymene, an aromatic hydrocarbon frequently found as the final transformation product of many terpene derivatives. To explain this reaction, the following formula was suggested:



which would appear to locate the relative positions of the methyl and isopropyl groups, but leaves the position of the unsaturation undetermined. The location of the double bond was deduced from the apparent formation of iso-valerianic acid on oxidation. Semmler² also reported this acid as an oxidation product of the aldehyde, but this was found later to be erroneous.

In 1896, citronellal was made the subject of an investigation by Tiemann



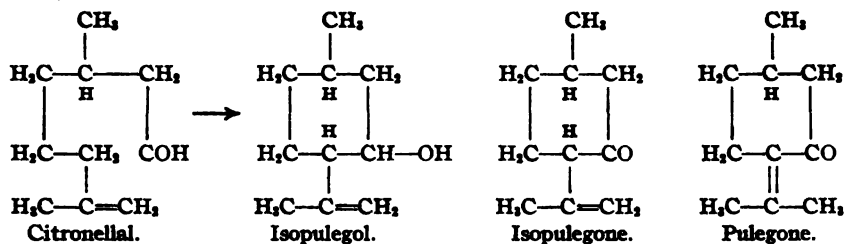
¹ *Am. Chem. J.*, 11, 456 (1889).

² *Ber.*, 24, 201 (1891).

and Schmidt.¹ By careful progressive oxidation, they obtained methyl adipic acid and acetone, which result pointed to the above formula.

There are, however, reasons for believing the double bond to be (8)-(9), and that a rearrangement occurs during the oxidation.

The conversion of citronellal into a cyclic isomer was also accomplished by Tiemann and Schmidt, and its relation to the menthol group was thus established, the structure of isopulegone being subsequently cleared up by Harries and Roeder.²



Among the products of the action of phosphoric anhydride on citronellal, the writer found a crystalline acid, containing phosphorus.³ This compound, called provisionally "citronellal phosphoric acid," but which now might more properly be termed "isopulegol phosphonic acid," has the composition, $\text{C}_{10}\text{H}_{19}\text{PO}_4$, and is formed when phosphoric anhydride acts on citronellal, in presence of a little water, as, e. g., in moist ether solution:



The most favorable conditions for the reaction have not yet been determined, the yield being at best about 25% of the theoretical.

This compound is a strong monobasic acid, yielding a series of well-defined salts, which are, in general, remarkably crystalline. It is difficultly soluble in water, but easily in alcohol and chloroform, and melts at $181-182^\circ$. From alcohol, the acid crystallizes in large, transparent plates, which were examined by the writer, in 1891, in the laboratory of Prof. Rosenbusch, at Heidelberg.

System: Mono-symmetric.

$$a : b : c :: 1.9828 : 1 : 1.9745. \quad \beta = 57^\circ 50'.$$

Planes: (001) oP, (100) $\infty \bar{P}\infty$, (011) ∞ P.

The crystals are tabular, (001) being the principal plane. A plane of the orthodoma zone was observed on only one crystal. The substance however, possesses a well-defined cleavage according to this plane, from which the value of the axis a was calculated. No twinning was observed.

$$\begin{array}{lcl}
 \text{Angles: } (001) : (100) & 57^\circ 50' \\
 (001) : (011) & 59^\circ 6' 30'' \\
 (100) : (10\bar{1}) & 60^\circ 52' \\
 (011) : (0\bar{1}1) & 61^\circ 49' (\text{calc.})
 \end{array}$$

¹ *Ber.*, 29, 904 (1896).

² *Ibid.*, 32, 3357 (1899).

³ *Am. Chem. J.*, 12, 553 (1890).

The cleavage according to the basis is perfect, large sections of any desired thickness being readily obtained. There is also a well-defined cleavage according to (101) but none in the clinodomal zone. The plane of the optic axes is perpendicular to the plane of symmetry, and inclined to the basis. Double refraction, strong, negative. Horizontal dispersion, weak. The angle of the optic axes is small.

Salts.—The potassium salt is easily obtained, in large, transparent plates:

1.000 g. pure acid, titrated with 0.5 *N* KOH, required 8.55 cc. (calc. for $C_{10}H_{17}PO_3$, 8.55 cc.). The solution was allowed to crystallize in desiccator, and the product recrystallized, and dried in air. 1.147 g. at 100° lost 0.1976 g., or 17.2% (calc. for $KC_{10}H_{15}PO_4 \cdot 3H_2O$: 16.56%). The anhydrous salt yielded on ignition 43.44% KPO_3 ; calc. 43.38%.

Attempts to prepare a di-potassium salt were unsuccessful. The sodium salt also crystallizes in large plates, much resembling those of the acid. The alkaline salts are remarkably stable; no decomposition was noticed on long boiling of the aqueous solutions.

The magnesium salt is readily soluble in water, and the crystals are like the sodium salt; the calcium salt is less soluble, but crystallizes well from hot water. The silver salt is at first a curdy precipitate, which soon becomes crystalline, and under the microscope exhibits characteristic forms.

At the time of discovery, very little could be inferred as to the structure of this acid. The formula proposed was merely empirical. The reaction appeared to be peculiar to citronellal, yet the stability and general properties of the acid made it improbable that it could be considered a true member of the citronellal series.

In 1894, Marsh and Gardner¹ described two crystalline acids, obtained from camphene by reaction with phosphorus pentachloride, and subsequent hydrolysis: an α acid, $C_{10}H_{17}PO_3 \cdot \frac{1}{2}H_2O$ (m. p. about 160°), and a β acid, $C_{10}H_{17}PO_3$ (m. p. about 167°). These acids showed some resemblance to the compound from citronellal, yet were evidently different bodies, and their structure is still unexplained.

Tiemann's discovery of the isopulegol reaction, however, suggested the possibility that the acid might be really a derivative of isopulegol, or a similar cyclic nucleus, and a study of the decomposition of the sodium salt on heating showed that this was probably the case.



This decomposition proceeds smoothly, and at a comparatively low temperature. For example, 9 g. of the dry sodium salt, in a small distilling flask, were heated cautiously until white fumes appeared. After cooling, 5 g. water were added, and the mixture distilled to dryness. The residue was again heated to fumes, distilled with water, etc., until no more oil was obtained. The product, after redistillation with water,

¹ *J. Chem. Soc.*, 65, I, 35 (1894).

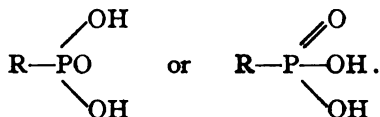
was a light colorless oil, with an odor resembling menthone. It was readily soluble in 70% alcohol, and by quantitative acetylation and saponification, showed an alcohol content of 92.5% $C_{10}H_{18}O$.

Chromic acid solution reacts immediately with the alcohol, and the oxidation product has the characteristic odor of pulegone. 1 g. treated with the calculated amount of chromic acid in 25 cc. of water, yielded, on steam distillation, 0.5 g. oil, which gave a well-crystallized semicarbazone, melting at about 171° . (Tiemann obtained from isopulegone a mixture of semi-carbazones, melting at 173° .)

The alcoholic product of the decomposition of the sodium salt is then most probably isopulegol, and the formation of the acid from citronellal is due to a ring-condensation analogous to that occurring with acetic anhydride.

As to the structure of the acid, the following points may be considered:

1. The acid is not hydrolyzed by hot alcoholic potassium hydroxide, nor by hot dilute sulfuric acid. Hence the PO_3 group is directly connected to carbon, and the compound must be regarded as a phosphonic acid,



Normal phosphonic acids are, however, dibasic, while the acid in question is sharply monobasic, and a di-potassium salt could not be prepared. It is to be noted that the camphene phosphonic acids of Marsh and Gardner¹ appear also to be monobasic.

2. The ready formation of isopulegol would lead to the assumption of a secondary hydroxyl group in the acid. Boiling acetic anhydride, however, leaves the acid unaltered; chromic acid and cold dilute permanganate are also without action, so that the presence of hydroxyl (except possibly in tertiary combination) seems improbable. Nor could any indications of a ketonic group be obtained: no oxime, or phenylhydrazone could be prepared from the acid. Moreover, if a CO group were present, menthone, or an isomeric ketone should result from the decomposition of the alkaline salt.

3. Isopulegol behaves as an unsaturated secondary alcohol, but the phosphonic acid appears to be a saturated compound. A solution of the sodium salt does not decolorize bromine water in the cold, nor, as already mentioned, does it reduce a weak permanganate solution. On heating with bromine water, a slow reaction occurs, and some of the acid crystallizes out unchanged.

The position of the phosphonic group is, of course, unknown, and the data available will hardly warrant further conjectures as to the molecu-

¹ *Loc. cit.*

lar design of this acid. It is evident, however, that isopulegol phosphoric acid is a peculiarly characteristic derivative of citronellal. The rearrangement of the open-chain aldehyde to a cyclic secondary alcohol is unique and the fact that no other aldehyde so far examined has yielded an analogous compound, is easily explained.

It appeared, then, not improbable that this reaction might be utilized for the detection of citronellal in oils in the presence of other aldehydes, especially as so far no very satisfactory method has been suggested.

For example, we find, as frequently occurring constituents of various essential oils, three closely related aldehydes:

- | | | |
|---------------------|--------------------------------------|--------------------|
| 1. Decylic aldehyde | $C_{10}H_{20}O$ (saturated) | (normal chain) (?) |
| 2. Citronellal | $C_{10}H_{18}O$ (unsaturated) | (terpene chain) |
| 3. Citral | $C_{10}H_{16}O$ (doubly unsaturated) | (terpene chain) |

The first has been found in the oils of orange, citronella, and ginger; the second, in the oils of citronella, eucalyptus, and lemon; the third, in oils of lemon, orange, lemongrass, verbena, etc.

The separation of these aldehydes can be accomplished by utilizing their varying behavior with bisulfite solution. The saturated decylic aldehyde forms a normal compound, $Ald.NaHSO_3$, slightly soluble, and decomposed by sodium carbonate. Citronellal also yields the normal $Ald.NaHSO_3$, with similar properties, but, on warming with excess of bisulfite, or in dilute acid solution, a sulfonate is formed, which is not decomposed by sodium carbonate or hydroxide. Citral forms at least three compounds: in cold, acid solution, $Ald.NaHSO_3$, unstable, decomposed by sodium carbonate; in cold, strongly alkaline solution, $Ald.2NaHSO_3$, very soluble, decomposed by cold hydroxide, not by carbonate; in warm acid solution, $Ald.2NaHSO_3$, not decomposed by carbonate nor hydroxide.

Hence, if we treat a mixture of the aldehydes (or an oil containing them) with a solution of sodium sulfite, containing some bicarbonate (to neutralize the alkali liberated), citral dissolves, and can be recovered, in good yield from the solution, by treatment with cold, strong sodium hydroxide. From the portion insoluble in neutral sulfite, decylal and citronellal can then be precipitated by slightly acid bisulfite, in the cold. If the solution is heated, citronellal redissolves slowly and permanently, while the normal bisulfite compound of the saturated aldehyde generally crystallizes from the solution on cooling. From the crystals, decylic aldehyde can be obtained by careful treatment with bicarbonate.¹

In this way, citral and decylic aldehyde can generally be isolated and identified without much difficulty, but citronellal cannot be recovered from the solution, and the positive detection of the latter in the presence of a saturated aldehyde appears impracticable.

¹ Dodge, 8th Congr. Appl. Chem., 6, 77 (1912).

The occurrence of citronellal in oil of lemon has been reported by various observers. Doebner,¹ applying his general aldehyde reaction with pyroracemic acid and β -naphthylamine, obtained a mixture of crystalline naphthocinchoninic acids, which could be separated into the citral derivative, melting at 197°, and the citronellal derivative, melting at 225°, the latter in larger amount. Tiemann² fractionated the oil, and from the high-boiling sections, by the sulfite method, could isolate a small amount of aldehyde, identified as citronellal by the naphthocinchoninic acid. The amount present was estimated at 0.4% (or about $1/10$ of the citral). Schimmel and Co.³ consider the average aldehyde content of the oil to be: citral, 4.8%; citronellal, 1.2%. Burgess,⁴ however, was unable to confirm the presence of citronellal, but found a small amount of a lower saturated aldehyde, apparently octoic aldehyde. von Soden and Rojahn,⁵ from 10 kg. of oil, obtained besides citral, 10–15 g. of a mixture of aldehydes, apparently octoic and nonoic aldehydes and citronellal.

It appears possible that the relatively large amount of citronellal found by Doebner may be due to a confusion with the lower aldehydes, the presence of which was at that time unsuspected. Or, on the other hand, there may be a considerable loss of citronellal involved in the sulfite separation used by Tiemann, and von Soden and Rojahn.

In the hope of obtaining further information on this point, the phosphoric reaction described above was tried on the natural oil of lemon, and also on the commercial concentrated oil, containing 45–50% aldehydes, but in neither case could the formation of the isopulegol phosphonic acid be detected, and the conclusion appears warranted that the citronellal content of oil of lemon is quantitatively insignificant.

Summary.

The writer has made a further examination of the crystalline acid, containing phosphorus, resulting from the reaction of phosphoric anhydride on citronellal.

The compound is very stable, and yields a series of well-crystallized salts. By dry distillation of the sodium salt, a volatile alcohol was obtained, apparently identical with the isopulegol of Tiemann, a cyclic isomer of citronellal. The acid is then most probably a phosphonic acid of isopulegol, and hence a very characteristic derivative of citronellal.

Attempts to demonstrate the presence of citronellal in oil of lemon, by means of this reaction, were unsuccessful.

BAYONNE, N. J.

¹ *Arch. Pharm.*, 232, 688 (1894).

² *Ber.*, 32, 822 (1899).

³ *S. & Co., Ber.*, 1900, Oct. 25.

⁴ *J. Chem. Soc.*, 79, 171 (1901).

⁵ *Ber.*, 34, 2809 (1901).

[FROM THE DEPARTMENT OF ANIMAL HUSBANDRY OF THE UNIVERSITY OF ILLINOIS.]
**THE QUANTITATIVE DETERMINATION OF THE AMINO ACIDS
OF FEEDINGSTUFFS BY THE VAN SLYKE METHOD.**

[SECOND PAPER.]

BY H. S. GRINDLEY AND M. E. SLATER
with the collaboration of H. C. ECKSTEIN AND J. C. ROSS.

Received October 4, 1915.

Introduction.

In a previous paper¹ we have reported quantitative determinations of the amino acids of feedingstuffs made by the Van Slyke method. Additional results are presented in this paper. For easy reference and comparison, the analytical data for the three feeds—cottonseed meal, tankage, and alfalfa hay—previously reported are also included in Tables I and II, given below. The duplicate or triplicate results reported for the same feedingstuff were obtained from independent hydrolyses of the same sample. The figures for each individual constituent represents the average of two, three, or more determinations upon the same hydrolyzed solution.

Since the publication of our first paper, Nollau,² of the Kentucky Agricultural Experiment Station, has published a paper giving the amino-acid content of certain commercial feedingstuffs. On the whole, the results from the two laboratories do not agree well. In some determinations the results from the two sources are quite satisfactory, but in many cases the agreement is far from satisfactory. The lack of concordant results is due, in part at least, to differences in the details of procedure.

In the first place, Nollau removed the fat by extracting the finely ground feedingstuff with ether. In our work we did not remove the fat except in the case of tankage. It is impossible to say definitely, at the present time, how this difference in procedure would lead to differences in the amino-acid determinations.

In the second place, Nollau, in most of the feedingstuffs, filtered the hydrolyzed solution to remove the solid residue before concentrating under reduced pressure. The syrupy residue that was left after removing the excess of hydrochloric acid was dissolved in water, and the solution diluted to 250 cc. The total nitrogen determined in this solution was the basis for the calculation of the final results for the distribution of the nitrogen. By this method part of the total nitrogen of the feedingstuffs was removed and the quantity thus discarded was not determined. This procedure would lead to low humin-nitrogen figures and correspondingly high values for the remaining forms of nitrogen, considered on the basis of the total nitrogen of the feedingstuffs. Further, this method of analysis fails

¹ H. S. Grindley, W. E. Joseph and M. E. Slater, *THIS JOURNAL*, 37, 1778 (1915).

² *J. Biol. Chem.*, 21, 611 (1915).

to give results for the distribution of the total nitrogen in the feedingstuffs, and, therefore, such results cannot be used to calculate the nitrogen of the amino acids in terms of the feedingstuffs, since an undetermined part of the nitrogen of the samples was discarded.

By our method of procedure the hydrolyzed solution was not filtered before removing the excess of hydrochloric acid, or before determining the total nitrogen, the ammonia nitrogen, or the humin nitrogen. Therefore, we were able to calculate the nitrogen of the amino acids in per cent. of the feedingstuffs.

In the third place, there was evidently a difference in the details of the method for the determination of the organic sulfur in the two laboratories, for the cystine values of Nollau are two to four times greater than ours. These differences in the cystine values often, but not in all cases, make Nollau's lysine values considerably less than those obtained in this laboratory.

In the fourth place, the results for the nonamino nitrogen of the filtrate, as obtained in the two laboratories, clearly indicate a difference in the method of procedure in this determination. The nature of the difference is not evident at present.

Notwithstanding these marked discrepancies between the amino-acid determinations of the two laboratories, we feel confident from the results so far obtained that the Van Slyke method for the determination of the chemical groups characteristic of the amino acids of proteins will prove of much value as applied to the quantitative determination of the free and combined amino acids and amides of feedingstuffs when we become better acquainted with the details of the method, and succeed in adapting it to the specific conditions involved. At any rate, as yet, it is the only method that has been used for the determination of the amino-acid content of feedingstuffs, and, since it undoubtedly gives approximately quantitative results, it should, until some better method is developed, be used in gaining knowledge, that will aid us in applying to the economic and nutritive valuation of the common feedingstuffs, the fast accumulating results as to the nutritive value of the amino acids.

In this connection it may be well to call attention again to the fact that the object of the work reported in this paper and the preceding paper is to determine the free and the combined amino acids and the free and combined amides of feedingstuffs, and not merely the amino acids and the amides resulting from the hydrolysis of the proteins of the feedingstuffs.

Variations in the Percentages of Amino Acids in Feedingstuffs.

There are evidently marked variations in the free and combined amino-acid content of the common feedingstuffs. This variation can be clearly and readily seen from Table III, which gives the order of the feedingstuffs

according to their increasing content of the different forms of the nitrogen, determined by the Van Slyke method and expressed in percentage of the total nitrogen of the feedingstuff.

TABLE I.—THE NITROGEN OF THE AMINO ACIDS OF FEEDINGSTUFFS.

Results Expressed in Percentage of the Total Nitrogen of the Feedingstuffs.

Feedingstuff.	Ammonia N.	Humin N.	Arginine N.	Cystine N.	Histidine N.	Lysine N.	Amino N. in filtr. from bases.	Non-amino N. in filtr. from bases.	Total N. by summation.
Blood meal.....	5.98	3.90	9.47	0.70	8.45	9.89	55.21	4.73	98.33
Blood meal.....	5.74	3.81	8.97	0.68	8.52	9.59	57.29	4.32	98.92
Blood meal.....	5.83	3.83	9.04	0.68	8.63	9.70	57.20	4.21	99.12
Average.....	5.85	3.95	9.16	0.69	8.53	9.73	56.57	4.42	98.80
Tankage.....	6.52	4.40	14.38	1.27	5.15	7.52	52.36	7.27	98.87
Tankage.....	6.56	4.50	14.18	1.24	4.76	7.64	52.57	7.17	98.62
Tankage.....	6.66	4.30	13.88	1.32	4.91	7.28	52.24	7.38	97.97
Average.....	6.58	4.40	14.15	1.28	4.94	7.48	52.39	7.27	98.49
Wheat.....	17.71	9.24	7.72	1.37	1.71	2.56	46.81	12.32	99.44
Wheat.....	17.48	8.98	7.89	1.33	1.77	2.44	48.50	13.88	102.27
Wheat.....	17.57	9.40	8.37	1.32	1.54	2.41	47.69	14.58	102.88
Average.....	17.59	9.21	7.99	1.34	1.67	2.47	47.67	13.59	101.53
Rolled wheat.....	17.02	9.08	8.10	1.64	3.29	2.42	47.89	13.86	103.30
Rolled wheat.....	17.05	8.99	8.29	1.67	3.12	2.53	47.51	14.04	103.20
Average.....	17.04	9.04	8.20	1.66	3.21	2.48	47.70	13.95	103.28
Barley.....	15.21	8.79	9.16	1.16	3.77	1.64	45.82	13.86	99.41
Barley.....	15.11	8.78	9.75	1.36	3.51	2.73	45.80	13.81	100.85
Average.....	15.16	8.79	9.46	1.26	3.64	2.19	45.81	13.84	100.15
Oats.....	12.98	9.94	11.46	1.18	4.42	3.36	51.27	7.85	102.46
Oats.....	13.13	9.93	11.37	1.14	4.22	3.61	52.17	7.94	103.51
Average.....	13.06	9.94	11.42	1.16	4.32	3.49	51.72	7.90	103.01
White soy beans..	10.15	6.56	12.74	0.66	5.88	6.08	49.71	8.66	100.41
White soy beans..	10.09	6.69	12.60	0.67	5.65	6.20	49.86	8.45	100.21
Average.....	10.12	6.63	12.67	0.67	5.77	6.14	49.79	8.56	100.35
Cottonseed meal..	10.46	7.65	19.33	0.62	5.28	5.81	42.61	5.74	97.50
Cottonseed meal..	10.30	7.78	19.49	0.65	4.90	4.33	42.04	5.30	94.79
Cottonseed meal..	10.59	7.91	19.74	0.67	6.23	4.21	43.80	5.26	98.41
Average.....	10.45	7.78	19.52	0.65	5.47	4.78	42.82	5.43	96.90
Alfalfa hay.....	8.46	15.54	7.72	0.79	7.39	4.08	43.88	10.14	98.00
Alfalfa hay.....	8.42	16.03	7.64	0.97	7.49	4.12	44.15	9.43	98.15
Average.....	8.44	15.79	7.68	0.88	7.44	4.10	44.02	9.79	98.14

The Humin-Nitrogen Content of Feedingstuffs.

From even a casual inspection of the results for the amino acids of feedingstuffs, given in Table I, it is evident that the humin-nitrogen results are unusually high, with the exception of those for blood meal and tank-

TABLE II.—THE NITROGEN OF THE AMINO ACIDS OF FEEDINGSTUFFS.

Results Expressed in Percentage of the Feedingstuff.

Feedingstuff.	Ammonia N.	Humin N.	Arginine N.	Cystine N.	Histidine N.	Lysine N.	Amino N in filtr. from bases.	Non-amino N in filtr. from bases.	Total N by summation.	Total N by analysis.
Blood meal.....	0.837	0.546	1.325	0.098	1.041	1.383	7.724	0.662	13.616	13.988
Blood meal.....	0.803	0.534	1.255	0.095	1.191	1.342	7.907	0.604	13.731	13.988
Blood meal.....	0.815	0.536	1.264	0.095	1.305	1.356	7.982	0.589	13.942	13.988
Average.....	0.818	0.539	1.281	0.096	1.179	1.360	7.871	0.618	13.762	13.988
Tankage.....	0.653	0.440	1.439	0.128	0.516	0.753	5.238	0.729	9.896	10.013
Tankage.....	0.657	0.451	1.420	0.124	0.477	0.765	5.264	0.718	9.876	10.013
Tankage.....	0.667	0.430	1.390	0.132	0.492	0.729	5.213	0.739	9.782	10.013
Average.....	0.659	0.440	1.416	0.128	0.495	0.749	5.238	0.729	9.854	10.013
Wheat.....	0.383	0.200	0.167	0.030	0.037	0.055	1.010	0.266	2.148	2.160
Wheat.....	0.378	0.194	0.171	0.029	0.038	0.053	1.048	0.300	2.211	2.160
Wheat.....	0.380	0.203	0.181	0.029	0.033	0.056	1.030	0.315	2.227	2.160
Average.....	0.380	0.199	0.173	0.029	0.036	0.055	1.029	0.294	2.195	2.160
Rolled wheat.....	0.276	0.147	0.131	0.027	0.054	0.040	0.774	0.225	1.674	1.620
Rolled wheat.....	0.276	0.146	0.134	0.027	0.050	0.041	0.770	0.228	1.672	1.620
Average.....	0.276	0.147	0.133	0.027	0.052	0.041	0.772	0.227	1.675	1.620
Barley.....	0.360	0.208	0.217	0.027	0.089	0.039	1.085	0.328	2.353	2.368
Barley.....	0.358	0.208	0.231	0.032	0.083	0.065	1.085	0.327	2.389	2.368
Average.....	0.359	0.208	0.224	0.030	0.086	0.052	1.085	0.328	2.372	2.368
Oats.....	0.285	0.218	0.252	0.026	0.097	0.074	1.126	0.173	2.251	2.196
Oats.....	0.289	0.218	0.250	0.025	0.093	0.080	1.146	0.174	2.275	2.196
Average.....	0.289	0.218	0.251	0.026	0.095	0.077	1.136	0.174	2.264	2.196
White soy beans..	0.579	0.374	0.727	0.037	0.335	0.347	2.834	0.494	5.727	5.702
White soy beans..	0.576	0.381	0.725	0.038	0.322	0.354	2.843	0.482	5.721	5.702
Average.....	0.578	0.378	0.726	0.038	0.329	0.351	2.839	0.488	5.727	5.702
Cottonseed meal..	0.702	0.514	1.298	0.041	0.355	0.390	2.862	0.385	6.547	6.694
Cottonseed meal..	0.692	0.522	1.309	0.044	0.329	0.291	2.824	0.356	6.367	6.694
Cottonseed meal..	0.711	0.531	1.326	0.045	0.418	0.283	2.941	0.353	6.608	6.694
Average.....	0.702	0.522	1.311	0.043	0.367	0.321	2.876	0.365	6.507	6.694
Alfalfa hay.....	0.221	0.408	0.203	0.021	0.194	0.107	1.160	0.248	2.553	2.628
Alfalfa hay.....	0.222	0.421	0.201	0.023	0.197	0.108	1.153	0.266	2.593	2.628
Average.....	0.222	0.415	0.202	0.022	0.196	0.108	1.157	0.257	2.579	2.628

age, as compared with those for the pure isolated proteins. The highest humin nitrogen reported by Van Slyke¹ for pure proteins was 3.6% in the case of ox hemoglobin. Hartley² reported 2.5% of humin nitrogen in euglobulin of ox serum. Our results for humin nitrogen in feedingstuffs, excepting blood meal and tankage, are from two to four and one-

¹ *J. Biol. Chem.*, 10, 54 (1911).

² *Biochem. J.*, 8, 543 (1914).

TABLE III.—THE ORDER OF THE FEEDINGSTUFFS ACCORDING TO THEIR INCREASING CONTENT OF THE DIFFERENT FORMS OF NITROGEN DETERMINED BY THE VAN SLYKE METHOD AND EXPRESSED IN PERCENTAGE OF THE TOTAL NITROGEN OF THE FEEDINGSTUFF.

Ammonia N.		Melanine N.		Arginine N.	
Blood meal.....	5.85	Blood meal.....	3.85	Alfalfa hay.....	7.68
Tankage.....	6.58	Tankage.....	4.40	Whole wheat.....	7.99
Alfalfa hay.....	8.44	White soy beans ...	6.63	Rolled wheat.....	8.20
White soy beans...	10.12	Cottonseed meal ...	7.78	Blood meal.....	9.16
Cottonseed meal...	10.45	Barley.....	8.79	Barley.....	9.46
Oats.....	13.06	Rolled wheat.....	9.04	Oats.....	11.42
Barley.....	15.16	Whole wheat.....	9.21	White soy beans...	12.67
Rolled wheat.....	17.04	Oats.....	9.94	Tankage.....	14.15
Whole wheat.....	17.59	Alfalfa hay.....	15.79	Cottonseed meal....	19.52
Histidine N.		Cystine N.		Lysine N.	
Whole wheat.....	1.67	Cottonseed meal....	0.65	Barley.....	2.19
Rolled wheat.....	3.21	White soy beans....	0.67	Whole wheat.....	2.47
Barley.....	3.64	Blood meal.....	0.69	Rolled wheat.....	2.48
Oats.....	4.32	Alfalfa hay.....	0.88	Oats.....	3.49
Tankage.....	4.94	Oats.....	1.16	Alfalfa hay.....	4.10
Cottonseed meal...	5.47	Barley.....	1.26	Cottonseed meal....	4.78
White soy beans...	5.77	Tankage.....	1.28	White soy beans....	6.14
Alfalfa hay.....	7.44	Whole wheat.....	1.34	Tankage.....	7.48
Blood meal.....	8.53	Rolled wheat.....	1.66	Blood meal.....	9.73
Amino N in the filtrate from the bases.		Non-amino-N in the filtrate from the bases.			
Cottonseed meal.....	42.82	Blood meal.....	4.42		
Alfalfa hay.....	44.02	Cottonseed meal.....	5.43		
Barley.....	45.81	Tankage.....	7.27		
Whole wheat.....	47.67	Oats.....	7.90		
Rolled wheat.....	47.70	White soy beans....	8.56		
White soy beans....	49.79	Alfalfa hay.....	9.79		
Oats.....	51.72	Whole wheat.....	13.59		
Tankage.....	52.39	Barley.....	13.84		
Blood meal.....	56.57	Rolled wheat.....	13.95		
Diamino acid N.		Monoamino Acid N.			
Whole wheat.....	13.47	Cottonseed meal.....	48.25		
Rolled wheat.....	15.54	Alfalfa hay.....	54.81		
Barley.....	16.55	White soy beans....	58.35		
Alfalfa hay.....	20.10	Oats.....	59.62		
Oats.....	20.39	Tankage.....	59.66		
White soy beans....	25.25	Barley.....	59.69		
Tankage.....	27.88	Blood meal.....	60.99		
Blood meal.....	28.11	Whole wheat.....	61.26		
Cottonseed meal....	30.42	Rolled wheat.....	61.65		

half times greater than the result of Van Slyke for ox hemoglobin. Van Slyke found 7.42% of humin nitrogen in dog's hair.

The high humin results are undoubtedly due, in part at least, to the presence of soluble carbohydrates, judging from the researches of Gortner

and Blish¹ and of Maillard² and, possibly also to glycerol formed from fats by hydrolysis, judging from the researches of Maillard.³

Gortner and Blish have shown that the humin nitrogen of 0.5 g. of pure zein was increased from 0.46 to 1.84% by the presence of 0.50 g. of pure dextrose during the hydrolysis of the protéin. They have further demonstrated that the humin nitrogen of 1 g. of pure gliadin was increased from 0.59 to 0.94 per cent. by the presence of 0.25 g. of pure dextrose, and from 0.59 to 2.30 per cent. by the presence of 2.0 g. of dextrose, during the hydrolysis. Gortner and Blish have also demonstrated that when tryptophane was boiled with mineral acid in pure solution no humin was formed, but when tryptophane was added to a protein, or when carbohydrates were present, an abundance of humin was formed. When an abundance of carbohydrate was present, they found that 86% of the tryptophane nitrogen remained in the humin-nitrogen fraction.

The experiments of Osborne, Van Slyke, Leavenworth, and Vinograd⁴ have confirmed the results of Gortner and Blish in proving, first, that tryptophane when boiled with 20% hydrochloric acid in pure solution does not form humin, second, that tryptophane when boiled with 20% hydrochloric acid in the presence of glucose yields 86% of its nitrogen in the form of humin, and third, that the presence of glucose during hydrolysis increases the humin content of proteins. They found that the presence of glucose increased the humin content of lactalbumin from about 2.32 to 3.70%.

Maillard has apparently demonstrated that the amino acids, in general, readily react with the sugars in water solutions at temperatures from 100° to 150°, or below, to form humin-like substances that contain nitrogen. Further, this investigator claims that glycerol acts upon amino acids at increased temperatures, forming polypeptides, and that a secondary product possessing humin-like properties is produced.

It is not clearly apparent from the publications of Maillard that such reactions as he maintains take place between amino acids and carbohydrates and between amino acids and glycerol would occur in strong acid solutions such as those used in the hydrolysis of proteins, but it seems probable that the humin substances would be produced under such conditions.

Unfortunately, for the good of the methods for the analysis of proteins, the conclusion of Gortner and Blish, that in all probability the humin nitrogen of protein hydrolysis has its origin in the tryptophane nucleus, is apparently not true, since humin contains in addition adsorbed nitrogen from other amino acids. That their conclusion is probably

¹ THIS JOURNAL, 37, 1630 (1915).

² *Compt. rend.*, 154, 66-68 (1912); and *Compt. rend. Biol.*, 72, 599-601 (1912).

³ *Compt. rend.*, 153, 1078-1080 (1911); and *Compt. rend. Biol.*, 71, 546-549 (1911).

⁴ *J. Biol. Chem.*, 22, 259 (1915).

not true seems apparent from the researches of Maillard. Further, we have obtained results that clearly indicate that, in addition to tryptophane, a number of other amino acids, when gently boiled with 20% hydrochloric acid for 24 to 36 hours in the presence of pure glucose give humin nitrogen. Preliminary experiments show that under the above treatment 4.7 and 6.3% of the total nitrogen of lysine and cystine, respectively, is separated as humin nitrogen. These results, when confirmed by experiments now under way, will be published in full.

From the results of Gortner and Blish, and from our experiments, it seems somewhat probable that tryptophane enters into chemical combination with carbohydrates as suggested by Gortner and Blish, and that the other amino acids are to a greater or less extent adsorbed by the humin substances formed by the action of mineral acids upon carbohydrates. The fact, that in the experiments of Gortner and Blish, the humin nitrogen of zein, a tryptophane-free protein, was increased from 0.46 to 1.84% by the presence of 0.50 g. of dextrose during the hydrolysis, indicates that adsorption of amino acids had resulted.

The researches of Gortner and Blish, Maillard, and the authors of this paper, therefore, apparently show that the high humin nitrogen results we have obtained in the direct analysis of feedingstuffs by the Van Slyke method are due, in large part, to the presence of soluble carbohydrates during the hydrolysis of the proteins.

It is also possible that the high humin nitrogen which results during the analysis of feedingstuffs is due, in part, to the presence of cellulose which mechanically prevents the complete hydrolysis of the proteins. The results for the humin nitrogen given in Table III seem to indicate that such may be the case. Experiments are now being made to determine the completeness or incompleteness of the hydrolysis of the proteins of feedingstuffs containing relatively large amounts of crude fiber.

The high results for humin nitrogen obtained in this work constitute a source of error in the direct application of the Van Slyke method to the analysis of feedingstuffs, since, on the average, from 8 to 10% of the total nitrogen of the feedingstuffs is separated in the humin, which is an unknown mixture of secondary products, formed, probably, from a number of the amino acids resulting from the hydrolysis. Judging from the results for alfalfa hay, this error is greater for the roughages than for the concentrates. However, it is to be hoped, that further studies will make it possible either to reduce the quantity of nitrogen separated as humin, or to determine the quantities of nitrogen of the several amino acids represented in the humin fraction.

Summary.

1. The results here reported confirm the conclusion previously drawn, namely, that the Van Slyke method for the determination of the chem-

ical groups characteristic of the amino acids of proteins can be applied directly to the quantitative determinations of the amino acids of feeding-stuffs with at least a fair degree of accuracy.

2. The results which we have obtained for the quantitative determination of amino acids in feedingstuffs, on the whole, do not agree well with those recently published by Nollau. In some determinations the results from the two sources are quite satisfactory, but in many cases the agreement is far from satisfactory. The lack of concordant results is probably due in the main to differences in the details of procedure in the experimental work.

3. The results reported in this paper show that there are pronounced variations in the free and combined amino-acid content of the common feedingstuffs expressed in percentage of the total nitrogen. There are also wide and marked variations in the distribution of the nitrogen of the free and combined amino acids in the feedingstuffs, expressed in percentage of the feedingstuff.

4. It seems probable that the high results for humin nitrogen obtained in the direct analysis of feedingstuffs by the Van Slyke method are due, in part, to the presence of soluble carbohydrates during the hydrolysis of the proteins. It also seems probable that the high humin nitrogen which is obtained in the analysis of feedingstuffs may be due, in part, to the presence of cellulose, which mechanically prevents the complete hydrolysis of the proteins.

5. The high results for humin nitrogen constitute a source of error in the direct application of the Van Slyke method to the determination of the free and combined amino acids and amides of feedingstuffs.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY, No. 257.]

THE EFFECT OF SODIUM CHLORIDE UPON THE ACTION OF INVERTASE.

By H. A. FALES AND J. M. NELSON.

Received September 15, 1915.

The object of the work described in this paper is the study of the influence of sodium chloride upon the hydrolysis of cane sugar by invertase. The great susceptibility of the action of invertase to small amounts of acids and alkalies has been observed by Kjeldahl,¹ O'Sullivan and Thompson,² and others.

Sørensen³ made an important advance when he showed that the ac-

¹ *Meddelelser fra Carlsberg Laboratorit*, 1, 337 (1881).

² *J. Chem. Soc.*, 57, 835 (1890).

³ *Biochem. Ztg.*, 21, 131-304 (1909).

tivity of invertase is a function of the concentration of hydrogen ion rather than of the absolute amount of acid present. Furthermore, for any given concentration of hydrogen ion, the activity of the invertase is independent of the nature of the anion furnished by the acids that he tried, namely, hydrochloric, sulfuric, phosphoric and citric. He also measured the particular concentration of hydrogen ion at which invertase exhibits its maximum activity, and found it to be in the neighborhood of $10^{-4.5}$ mols hydrogen ion per liter at a temperature of 52.5° . We are greatly indebted to Sørensen for working out in detail the methods for the measurement of the concentration of hydrogen ion in enzymatic reactions in general. The results of Michaelis and Davidsohn¹ and of the present work confirm Sørensen's observations as to the optimum zone of invertase activity. One may, therefore, accept with reasonable assurance that the relationship existing between the concentration of hydrogen ion and the activity of invertase has been definitely determined.

As regards the effect of salts upon the activity of invertase, it seems that the most extensive work with this purpose in view is that of Cole,² but his results do not admit of any reliable conclusions because he did not record the concentration of hydrogen ion in his respective experiments. As he himself says:

"I have tried the effect of mixtures of HCl and chlorides on the action of invertin but the results have been very unexpected and difficult to interpret."

Michaelis and Davidsohn³ carried out one experiment with $M/710$ potassium chloride, but consider that the concentration of the potassium chloride is too small to exert any disturbing influence. They also tried an experiment with $M/225$ potassium chloride, and one with $M/150$ potassium chloride but they do not discuss their results with reference to the salt effect.

In view of the negative results of Cole and because of the recognized importance of the influence of salts in hydrolytic cleavage reactions in general,⁴ the authors of this paper deemed it advisable to start with the study of the effect of sodium chloride upon the activity of invertase in the hydrolysis of cane sugar. In the elaboration of the experimental detail, they have been guided by two main considerations: the one of theoretical interest to see if further insight could not be gained into the mechanism of the inversion of cane sugar; the other of practical value to determine whether the use of so-called "buffers" (mixtures of acids and salts) which many investigators employ to secure their desired concen-

¹ *Biochem. Ztg.*, 35, 386 (1911).

² *J. Physiol.*, 30, 281 (1904).

³ *Loc. cit.*

⁴ Vide Spohr, *Z. physik. Chem.*, 2, 194 (1888); Arrhenius, *Ibid.*, 4, 226 (1889); Euler, *Ibid.*, 32, 348 (1900).

tration of hydrogen ion, gives results which are comparable with those obtained for the same concentration of hydrogen ion secured by the use of acids or alkalies alone.

The general plan of procedure in this work has been to measure the activity of invertase at various concentrations of hydrogen ion ranging from $10^{-1.4}$ to $10^{-6.6}$, then to measure the activity over the same range of hydrogen ion concentrations in the presence of 0.1, 0.5 and 2 molar sodium chloride.

The relationship between the activity of invertase and hydrogen ion concentration has been found to be briefly as follows for the conditions given: total volume of solution, 100 cc.; amount of cane sugar, 0.500 g.; amount of invertase, 10 cc. of working solution of invertase;¹ concentration of hydrochloric acid, enough to give the desired concentration of hydrogen ion; temperature $37^{\circ} \pm 0.01^{\circ}$. For details, see experiments Nos. 2, 7, 11 and 17.

Value of $p_{H^{+}}$	1.4	3.1	3.3	4.5	6.0	6.3	6.5
Activity.....	None	75	85	94	51	33	26

The term $p_{H^{+}}$ is Sørensen's symbol for expressing the concentration of the hydrogen ion. The values are the negative exponents to which the number ten must be raised in order to equal the given concentration. Thus, $p_{H^{+}} = 4.5$ means that the concentration of hydrogen ion is equal to $10^{-4.5} = 0.00003$ mol hydrogen per liter. Since the values of $p_{H^{+}}$ represent negative exponents, it follows that the smaller the numerical value of $p_{H^{+}}$ the larger the concentration of hydrogen ion and *vice versa*; for 0.1 *M* hydrochloric acid $p_{H^{+}} = 1.04$, while for 0.1 *M* sodium hydroxide $p_{H^{+}} = 13.06$. The authors have found it very convenient to designate the symbol $p_{H^{+}}$ by the term "index" and it is employed in this sense throughout this article.

Armstrong and Armstrong² strongly object to indicating the concentration of hydrogen ion in this way, but it would seem that they are not fully familiar with the scheme as is evident from the following quotation from their article:

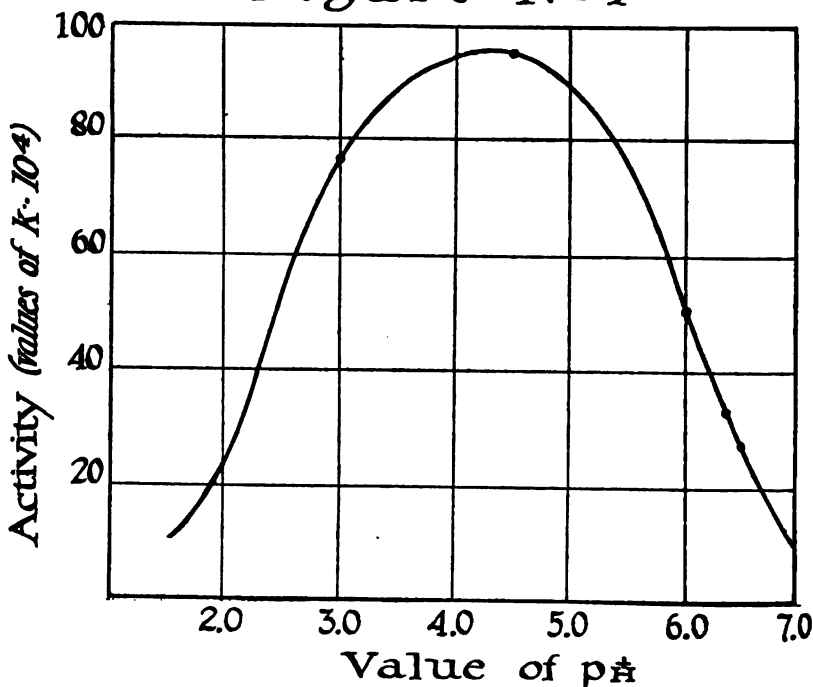
"It is difficult enough for nonmathematical readers to appreciate values stated in terms of the expression $x \times 10^{-7}$ or 10^{-9} but it is still more difficult for them to follow the method adopted by Sørensen, the first to introduce order, and one of the chief workers in this field, who uses the indices alone (the y values) as the exponents of the hydrogen-ion concentration, so that values below 7 indicate alkalinity and those above 7 acidity."

¹ Prepared each time as wanted by diluting 10 cc. of a stock solution of invertase to 100 cc. and then taking 10 cc. portions from this 100 cc. The stock solution was made from invertase prepared by Nelson and Born (*THIS JOURNAL*, 36, 393 (1914)) and contained 7 g. invertase per liter. It showed no decrease in activity after being kept for one year in the ice box.

² *Proc. Roy. Soc., (B)* 86, 576 (1913).

Activity.—The values in the activity column are the values of the velocity coefficients $\times 10^4$ calculated from the monomolecular equation $k = \frac{1}{t} \log \frac{a}{a-x}$ (A), where t is the time in minutes, and the logarithms are those to the base ten. It is to be pointed out that the values of the

Figure N° 1



velocity coefficients calculated from this equation differ somewhat from those calculated from the equation $k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$ (B). The use of Equation A seems to give smoother results. It is, therefore, necessary in comparing values obtained by different workers to see that they are evaluated by means of the same equation, as is evidenced by taking

Mins.	% In- version.	(A).	(B).	Mins.	% In- version.	(A).	(B).
5	3.1	0.0027	0.0031	182	74.5	0.0033	0.0036
15	9.8	0.0030	0.0032	210	79.8	0.0033	0.0037
30	19.2	0.0031	0.0032	240	84.4	0.0034	0.0030
57	33.6	0.0031	0.0027	270	87.3	0.0033	0.0026
90	45.8	0.0030	0.0039	381	93.5	0.0031	0.0025
120	58.5	0.0032	0.0035	430	95.1	0.0032 ¹	0.0016
150	67.4	0.0032	0.0033	508	96.3	0.0028 ¹	0.0007

¹ Calculated by the authors of this paper.

one of O'Sullivan and Thompson's experiments,¹ the results of which have been calculated by Hudson² according to (A) and by Sørensen¹ according to (B).

The above illustration has been cited because of the importance that the velocity coefficients have played in the discussions as to whether the inversion of cane sugar by invertase can be regarded strictly as a monomolecular reaction or not.

Effect of Salt.—In adjusting the acidity of the solutions for the tests at an index of 1.5, it was found that when the same amounts of hydrochloric acid were made up to the same volume with water and with solutions of sodium chloride so that the resulting concentration of sodium chloride was respectively 0.1, 0.5 and 2.0 *M*, the resulting indices of the solutions, as measured by the electromotive force method (described subsequently in this article) were in each case different, and in such wise that the greater the concentration of sodium chloride, the less the value of the index; or in other words, the greater the concentration of hydrogen ion.

Thus the following results were obtained, when in the final volume of the solution the concentration of the hydrochloric acid was 0.045 *M*. and the concentration of sodium chloride as given:

	No. salt.	0.1 <i>M</i> NaCl.	0.5 <i>M</i> NaCl.	2.0 <i>M</i> NaCl.
E. m. f. (volts) at 25°.....	0.4185	0.4160	0.4100	0.3936
Value of p_{H^+}	1.41	1.37	1.27	1.00
Conc. of hydrogen ion.....	0.039	0.043	0.054	0.100
% increase of H^+	10.3	38.5	156.0

This increase of hydrogen ion concentration seems also to be in line with the increase of the velocity coefficients obtained in the hydrolysis of cane sugar under the same conditions as regards concentration of hydrochloric acid and concentration of sodium chloride (see Experiments Nos. 1, 3 and 5) as is shown herewith:

	No. salt.	0.1 <i>M</i> NaCl.	0.5 <i>M</i> NaCl.	2.0 <i>M</i> NaCl.
Vel. coeff. at 37°. Conc. HCl 0.045 <i>M</i>	0.00073	0.00093	0.00176
% increase of vel. coeff.....	27.4	141.0

Loomis and Acree³ observed that the addition of potassium chloride to acetic acid solutions slightly increases the dissociation of the acetic acid, although the validity of their results has been questioned by McBain and Coleman.⁴ B. von Szyzkowski⁵ cites the fact, which the authors have also noticed, that methyl orange behaves as if the concentration of

¹ *Loc. cit.*

² *THIS JOURNAL*, 30, 1160 (1908).

³ *Am. Chem. J.*, 46, 621 (1911).

⁴ *J. Chem. Soc.*, 105, 1517 (1914).

⁵ *Z. physik. Chem.*, 78, 426 (1912).

hydrogen ion is increased when sodium chloride is added to a very dilute solution of hydrochloric acid. Poma¹ states that the presence of sodium chloride as well as the chlorides of other alkali metals increases the concentration of hydrogen ion of hydrochloric acid solutions.

Apart from whatever theoretical importance the above observation may have, it illustrates the necessity of actually measuring the concentration of hydrogen ion in all such experiments rather than calculating it from the molarity of the acid used and the concentration of the salt added.

In the experiments which follow (1-17) 10 cc. of cane sugar solution, containing 0.500 g. of cane sugar were used in every instance, together with the other additions as indicated. The temperature was $37 \pm 0.01^\circ$.

Effect at $p_{H^+} = 1.40$.—The results of the measurements of the activity of invertase at an index of 1.40 and less, show that invertase has no inverting action, irrespective of whether there is no sodium chloride, 0.1, 0.5 or 2.0 *M* sodium chloride present. (See Expts. 1 to 6 inclusive.)

TABLE I.

Expts. 1-6; 9 cc. of 0.5 *M* HCl added in every case, other additions as noted.

No. 1: 81 cc. water; $p_{H^+} = 1.41$ (e. m. f. 25°).

Minutes.....	180	210	225	255	285
Mg. cane sugar inverted.....	12.4	14.8	16.0	17.6	19.4
$K \times 10^4$ (acid alone).....	6.9	7.3	7.4	7.4	7.5

No. 2: +71 cc. water; +10 cc. invertase working solution containing 0.007 g. invertase; $p_{H^+} = 1.42, 1.43$ (e. m. f. 25°).

Minutes.....	180	210	225	255	285
Mg. cane sugar inverted.....	12.4	14.8	16.0	17.6	19.4
$K \times 10^4$	No inversion by invertase.				

No. 3: +31 cc. water; +50 cc. 1.0 *M* NaCl; $p_{H^+} = 1.27, 1.27$ (e. m. f. 25°).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	..	2.6	4.7	6.8	8.8	11.5
$K \times 10^4$ (acid + NaCl).....	..	7.7	9.5	10.6	9.3	9.5

No. 4: +21 cc. water; +50 cc. 1.0 *M* NaCl; +10 cc. invertase working solution containing 0.007 g. invertase; $p_{H^+} = 1.27, 1.27$ (e. m. f. 25°).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	..	2.6	4.7	6.8	8.8	11.5
$K \times 10^4$	No inversion by invertase.					

No. 5: +31 cc. water; +50 cc. 4.0 *M* NaCl; $p_{H^+} = 1.00; 1.00$ (e. m. f. 25°).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	2.0	5.3	8.5	11.7	15.1	19.1
$K \times 10^4$ (acid + NaCl).....	11.8	16.2	18.0	19.3	17.3	17.4

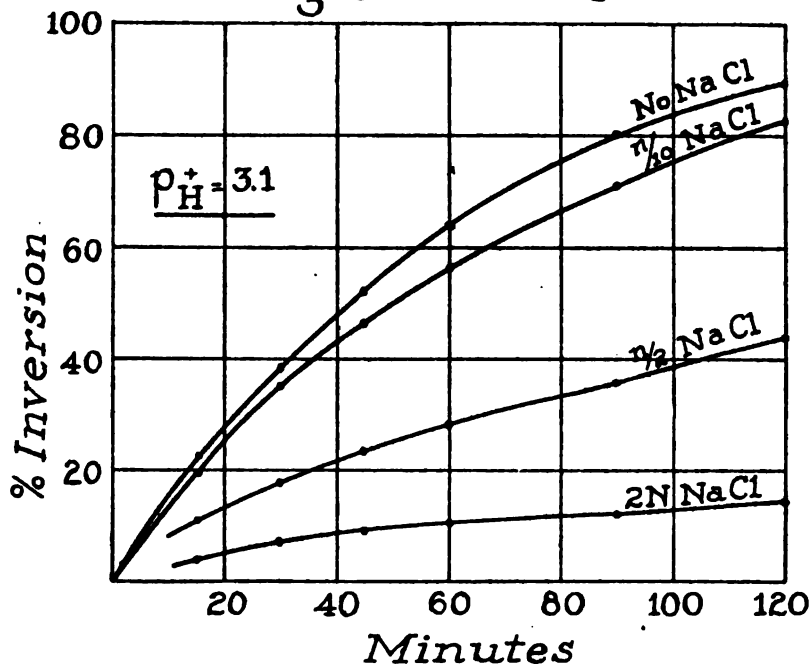
No. 6: +21 cc. water; +50 cc. 4.0 *M* NaCl; +10 cc. invertase working solution containing 0.007 g. invertase; $p_{H^+} = 1.00, 1.00$ (e. m. f. 25°).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	2.0	5.3	8.5	11.7	15.1	19.1
$K \times 10^4$	No inversion by invertase.					

¹ *Z. physik. Chem.*, 88, 641 (1914).

Effect at $p_{H^{+}} = 3.1$.—The results at an index of about 3.1 show a progressively retarding effect of the sodium chloride as evidenced by

Figure N^o 2



the following values, which are represented graphically in Fig. 2. For details, see Expts. 7, 8, 9 and 10.

PERCENTAGE INVERSION AT TIME GIVEN.

Mins.	No salt. $p_{H^{+}} = 3.1$.	0.1 M NaCl. $p_{H^{+}} = 3.2$.	0.5 M NaCl. $p_{H^{+}} = 3.1$.	2.0 M NaCl. $p_{H^{+}} = 3.0$.
15	22.4	19.8	11.8	4.0
30	39.6	34.0	18.4	8.0
45	52.8	46.0	23.0	8.2
60	64.6	57.4	28.4	10.4
90	80.6	70.1	35.0	12.2
120	89.0	82.6	44.0	13.8

TABLE II.

Expts. 7-10, incl.; 10 cc. cane sugar; 0.7 cc. 0.1 M HCl (except No. 10 with 0.5 cc.); 10 cc. invertase working soln. contg. 0.007 g. invertase; other additions as noted.

No. 7: +80 cc. water; $p_{H^{+}} = 3.2$, 3.2 (e. m. f. 25°); $p_{H^{+}} = 3.1$, 3.2 (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	11.2	19.8	26.4	32.3	40.3	44.5
$K \times 10^4$	73	73	73	75	79	80

TABLE II (continued).

No. 8: +70 cc. water; +10 cc. 1.0 *M* NaCl; $p_{\text{H}}^+ = 3.22, 3.22$ (e. m. f. 25°); $p_{\text{H}}^+ 3.3, 3.2$ (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	9.9	17.0	23.0	28.7	35.5	41.3
$K \times 10^4$	64	60	60	62	60	63

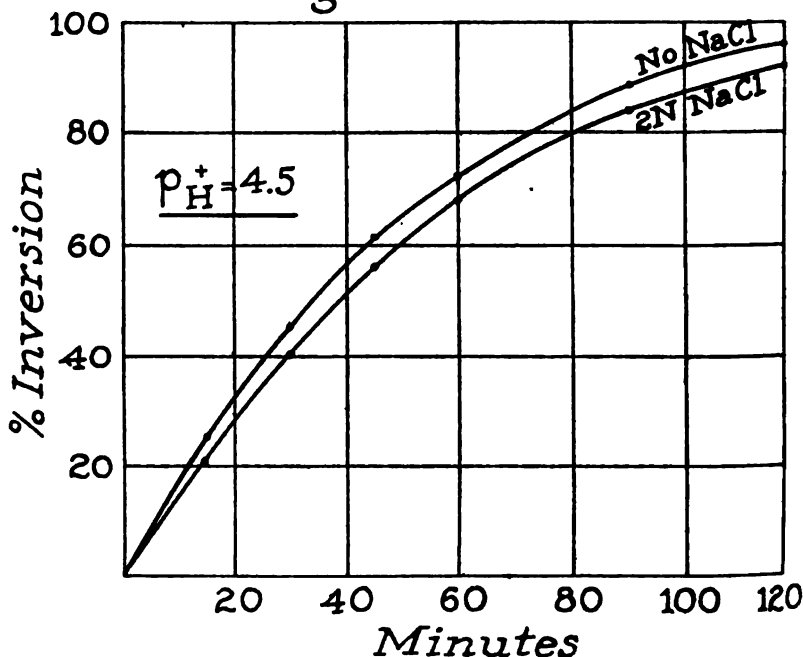
No. 9: +30 cc. water; +50 cc. 1.0 *M* NaCl; $p_{\text{H}}^+ = 3.0, 3.0$ (e. m. f. 25°); $p_{\text{H}}^+ = 3.1, 3.2$ (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	5.9	9.2	11.5	14.2	17.5	22.2
$K \times 10^4$	36	29	25	24	22	21

No. 10: +30 cc. water; +50 cc. 4.0 *M* NaCl; $p_{\text{H}}^+ = 3.0, 3.0$ (e. m. f. 25°); $p_{\text{H}}^+ = 2.7, 2.7$ (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	2.0	4.0	4.1	5.2	6.1	6.9
$K \times 10^4$	12	12	8	8	6	5

Effect at $p_{\text{H}}^+ = 4.5$.—The investigation of the salt effect at an index of 4.5 reveals the rather surprising result that in this region, sodium chloride, at least below the concentration of 2 molar, has very little effect upon the activity of invertase. The graphs (see Fig. 3) all lie so close together that only the one for no salt and the one for 2 molar sodium chloride have been drawn. The other two graphs are practically con-

Figure N^o 3

tained in the space between these two. For details, see Expts. 11, 12, 13 and 14.

PERCENTAGE OF INVERSION AT TIME GIVEN.

Mins.	No salt. $p_{H^+} = 4.6$.	0.1 M NaCl. $p_{H^+} = 4.4$.	0.5 M NaCl. $p_{H^+} = 4.6$.	2.0 M NaCl. $p_{H^+} = 4.5$.
15	25.8	26.0	25.8	20.8
30	45.2	45.1	44.2	40.0
45	62.6	60.0	61.0	57.6
60	72.8	72.6	72.6	68.2
90	87.2	86.6	88.8	84.4
120	94.6	96.6	95.4	92.0

TABLE III.

Expts. 11-14, incl.; 10 cc. cane sugar; +10 cc. invertase working soln. contg. 0.007 g. invertase; + other additions as noted.

No. 11: +80 cc. water; +1.1 cc. 0.01 M HCl; $p_{H^+} = 4.6$, 4.6 (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	12.9	22.6	28.7	36.4	43.6	47.3
$K \times 10^4$	86	87	95	94	99	106

No. 12: +70 cc. water; +10 cc. 1.0 M NaCl; +1 cc. 0.01 M HCl; $p_{H^+} = 4.5$, 4.5 (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	12.9	22.6	30.0	36.3	43.3	48.3
$K \times 10^4$	86	87	89	94	97	122

No. 13: +30 cc. water; +50 cc. 1.0 M NaCl; +0.7 cc. 0.1 M HCl; $p_{H^+} = 4.6$, 4.5 (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	12.9	22.1	30.5	36.3	44.4	47.7
$K \times 10^4$	86	84	91	94	106	111

No. 14: +30 cc. water; +50 cc. 4.0 M NaCl; +0.4 cc. 0.01 M HCl; $p_{H^+} = 4.1$, 4.3 (e. m. f. 25°); $p_{H^+} = 4.4$, 4.3 (by methyl orange).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	10.0	20.0	28.4	32.8	42.8	46.0
$K \times 10^4$	65	74	81	77	93	91

Effect at $p_{H^+} = 6.5$.—In the region having an index of about 6.5, the sodium chloride causes a decrease in the activity of the invertase much the same way that it does in the region having an index of 3.1. For details, see Expts. 15, 16 and 17.

PERCENTAGE INVERSION AT TIME GIVEN.

Mins.	No salt. $p_{H^+} = 6.5$.	0.1 M NaCl. $p_{H^+} = 6.4$.	0.5 M NaCl. $p_{H^+} = 6.5$.
15	11.6	9.0	4.8
30	19.2	15.2	8.6
45	24.0	19.8	12.6
60	29.6	25.2	16.4
90	42.4	33.6	21.6
120	51.0	40.8	26.8

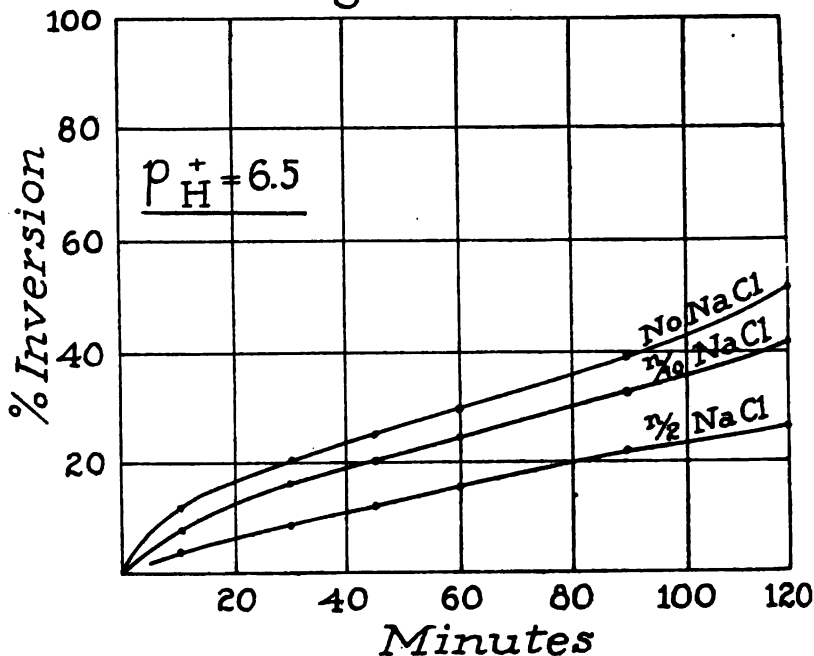
Figure N^o 4

TABLE IV.

Expts. 15-17, incl.; 10 cc. cane sugar; +10 cc. invertase working soln. contg. 0.007 g. invertase; + other additions as noted.

No. 15: +80 cc. water; $p_{H^+} = 6.5, 6.5$ (by rosolic acid).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	5.8	9.6	12.0	14.8	21.2	25.5
$K \times 10^4$	36	31	27	25	27	26

No. 16: +70 cc. water; +10 cc. 1.0 *M* NaCl; $p_{H^+} = 6.4, 6.4$ (by rosolic acid).

Minutes.....	15	30	45	60	90	120
Mg. cane sugar inverted.....	4.5	7.6	9.9	12.6	16.8	20.4
$K \times 10^4$	27	24	21	21	20	19

No. 17: +30 cc. water; +50 cc. 1.0 *M* NaCl; $p_{H^+} = 6.5, 6.5$ (by rosolic acid).

Minutes.....	15	30	45	60	90
Mg. cane sugar inverted.....	2.4	4.3	6.3	8.2	10.8
$K \times 10^4$	14	13	13	13	12

Discussion of Salt Effect.

A consideration of the above facts shows that the effect of the sodium chloride is twofold: first, it causes an increase in the concentration of hydrogen ion when the concentration of hydrochloric acid is greater than 0.0001 molar; secondly, it causes a decrease in the activity of the invertase, provided that in each case the concentration of hydrogen ion

is the same. This latter effect varies with the index of the solution and with the amount of sodium chloride added. It is least at the optimum and increases as we depart on either side from this optimum.

This shows that the use of buffers in large concentrations for regulating the index of the solution introduces more or less of an error if it is desired to get the maximum activity of invertase corresponding to a given concentration of hydrogen ion.

The foregoing results also disclose another very interesting feature upon examining the velocity coefficients calculated from them by means

of the equation $k = \frac{1}{t} \log \frac{a}{a-x}$. If the successive velocity coefficients

for any given test are considered, it will be noticed that one of the three following relationships applies: (1) the coefficients steadily increase in value; (2) they do not change; (3) they steadily decrease. That is to say, the acceleration may be either positive, zero, or negative during the course of the reaction.

TABLE V.

Values of $k \times 10^4$ when $p_{H^+} = 3.1$.

Minutes.....	15	30	45	60	90	120	
No NaCl.....	73	73	73	75	79	80	Increase of k
0.1 M NaCl.....	64	60	60	62	60	60	No change of k
0.5 M NaCl.....	36	29	25	24	22	21	Decrease of k
2.0 M NaCl.....	12	12	8	8	6	5	Decrease of k

Values of $k \times 10^4$ when $p_{H^+} = 4.5$.

No NaCl.....	86	87	94	94	99	106	Increase of k
0.1 M NaCl.....	87	87	89	94	97	122	Increase of k
0.5 M NaCl.....	86	85	91	94	106	122	Increase of k
2.0 M NaCl.....	67	74	83	83	90	91	Increase of k

Values of $k \times 10^4$ when $p_{H^+} = 6.5$.

No NaCl.....	36	31	27	25	27	26	Decrease of k
0.1 M NaCl.....	27	24	21	21	20	19	Decrease of k
0.5 M NaCl.....	14	13	13	13	12	11	Decrease of k

The progressive change in the value of k in those cases where it occurs cannot be ascribed to experimental error due to mutarotation, as Hudson¹ has pointed out is the case with Henri's results,² since a reduction method was used for the estimation of the amount of sugar inverted. Nor can it be ascribed to a change in the concentration of hydrogen ion of the solution taking place during the hydrolysis of the sugar, because repeated measurements in this regard showed that the concentration of hydrogen ion remained constant throughout the whole course of the inversion.

O'Sullivan and Thompson³ have noticed an increase in the value of k ,

¹ THIS JOURNAL, 30, 1564 (1908).

² Z. physik. Chem., 39, 194 (1902).

³ Loc. cit.; Tableaux 24-29.

up to a certain point, about 80% of inversion and after that a decrease. Sørensen gives five examples of increasing values and one of decreasing. Hudson's results¹ show a constant velocity coefficient and likewise those of A. Taylor,² while Michaelis and Davidsohn³ find increasing values.

It does not seem possible at present to find a generalization that will characterize this phenomenon of acceleration so as to bring into harmony the observations of the above investigators, because as is evident from our experiments the acceleration is affected by several variables. Thus in the absence of sodium chloride, a change in the concentration of hydrogen ion causes a change in the acceleration. In the presence of sodium chloride, if the concentration of hydrogen ion is kept constant, varying the concentration of the sodium chloride may or may not affect the acceleration.

For these reasons the results of different authors cannot be compared strictly in this regard, although the preponderance of evidence seems to show that an increase in the value of k with the progress of the reaction is what most investigators have encountered in studying the hydrolysis of cane sugar by means of invertase. These considerations obviously nullify the question put forth by Michaelis and Menton³ as to the reliability of the constancy of Hudson's coefficients.

Measurement of the Concentration of Hydrogen Ion.

In measuring the concentration of hydrogen ion, the electromotive force method⁴ and the colorimetric method⁵ were used.

In this regard it is to be pointed out that each method has certain inherent limitations. It is not possible to employ the electromotive force method when the index of the solution has a value lying between 3.7 and 9.0 and the solution is free from salt. This is on account of the fact that the resistance of the solution is so great under these circumstances that a fairly sensitive galvanometer (*i. e.*, one having a sensitivity of 20 megohms) scarcely gives a noticeable deflection when the circuit is closed. If, however, the solution contains a small amount of salt there is no trouble in making measurements in the region mentioned. Whether the index which is obtained in the presence of salt is exactly the same as the index of the solution without the salt is still a matter to be determined experimentally. It is usually assumed that the formula of Arrhenius⁶ holds, and that the addition of a neutral salt with an ion in common causes a repression of the ionization of the acid.

When the concentration of hydrogen ion is determined in the presence

¹ *Loc. cit.*

² *J. Biol. Chem.*, **5**, 405 (1909).

³ *Biochem. Z.*, **49**, 333 (1913).

⁴ Nernst, *Z. physik. Chem.*, **4**, 129 (1889).

⁵ Sørensen, *Loc. cit.*

⁶ *Z. physik. Chem.*, **31**, 204 (1899).

of salts by the colorimetric method the results vary more or less widely from the truth,¹ the amount of variation depending upon the particular indicator used and the kind and amount of salt present. Proteins and chloroform or toluene, used to prevent the growth of microorganisms, also have more or less influence.

The electromotive force measurements were all made at a temperature of 25°. The zero method was employed and the voltages obtained by means of a Leeds & Northrup potentiometer and a D'Arsonval galvanometer which had the following characteristics: a sensitivity of 280 megohms, a period of 2.5 seconds, and a total resistance of 444 ohms. As primary standard of potential a Weston standard cell, which had been calibrated by the Bureau of Standards, was used.

The voltages are those given by the combination $H_2 - Pt - H^+ - 3.5 M KCl - 0.1 M KCl - HgCl - Hg$ after correcting for the contact potential by Bjerrum's² method of extrapolation, which is to add, to the voltage obtained by using 3.5 M KCl as the salt bridge, the difference between this voltage and that obtained by using 1.75 M KCl as the salt bridge.

From the extrapolated voltage, the concentration of hydrogen ion was calculated by the equation

$$\log \text{conc. } H^+ = \frac{0.335 - \pi}{0.591} \text{ (valid only for } 25^\circ),$$

where π is the voltage obtained by extrapolation of the observed voltages according to Bjerrum's method.

The platinum electrodes were always checked up before use, by measuring the voltage given by a solution of 0.1 M HCl. This is a very important precaution, because if, as often happens, the observed voltage under these circumstances differs by more than a millivolt from the calculated, the platinum electrode (or possibly the calomel cell) is not working properly.

Adjustment of p_H^+ .—Attention must be called to the great influence that the character of the water used has in the adjustment of p_H^+ in the region $p_H^+ = 4.5$ to 6.0 by means of dilute hydrochloric acid. If buffers are used for this adjustment, there is no difficulty in regulating the concentration of hydrogen ion, but to offset this, there is introduced the salt effect due to the buffer.

While pure water has theoretically an index of 7.0 at 25°, it was not found possible to prepare any water having such an index. The ordinary distilled water used in this laboratory has given a fairly constant index around 6.2. When this water was distilled over Nessler solution and condensed through a tin condenser, the main portion of the distillate had an index of 5.8. When the water was distilled over alkaline permanganate, the index obtained was 5.8. Furthermore, when the water

¹ Cf. Sørensen, *Compt. rend. Laboratoire de Carlsberg*, Vol. 9 (1910).

² *Z. physik. Chem.*, 53, 428 (1905).

was distilled over alkaline permanganate and then over phosphoric acid, an index of 5.8 was obtained. In these tests the index was determined by using *p*-nitrophenol as indicator and mixtures of citrate solution and 0.1 molar sodium hydroxide as the comparison standards.¹

The following analyses show that the low index, in the case of the ordinary distilled water, and of the water distilled over Nessler solution, is probably caused by the carbonic acid present, although the observed indices of 6.2 and 5.8 are, respectively, higher than the calculated values of 5.2 and 5.5 figured from the amounts of carbonic acid present.

TABLE VI.

	(A). Ordinary distilled water.	(B). Water distilled over Nessler solution
Total solids.....	7.6 mg. per liter	4.0 mg. per liter
Loss upon ignition.....	4.8 mg. per liter	1.2 mg. per liter
Fixed solids.....	2.8 mg. per liter	2.8 mg. per liter
Total NH ₃	0.58 mg. per liter	0.03 mg. per liter
Free CO ₂	6.0 mg. per liter	2.2 mg. per liter
pH ⁺ (<i>p</i> -nitrophenol).....	6.2	5.8
Conductivity $\times 10^6$ recip. ohms.....	2.5	1.5

The results obtained by using the above two samples of water show the influence that the character of the water has upon the adjustment of pH⁺ at extreme dilutions of hydrochloric acid, as is evidenced by the following table. For indices less than 4.0 this effect disappears.

TABLE VII.

Cc. HCl in 100 cc.	Molarity of HCl.	Calc. values for pH ⁺ .	Obs. values for pH ⁺ .	
			(A).	(B).
0.1 cc. 0.01 <i>M</i>	0.00001	5.00	5.85	5.65
0.2	0.00002	4.70	5.7	5.4
0.4	0.00004	4.40	5.5	4.9
0.6	0.00006	4.22	5.3	4.4
0.8	0.00008	4.10	5.0	4.1
1.0	0.0001	4.0	4.6	4.0
2.0	0.0002	3.7	4.1	3.8
4.0	0.0004	3.4	3.4	3.4
0.6 cc. 0.1 <i>M</i>	0.0006	3.22	3.2	3.2
0.8	0.0008	3.10	3.1	3.1
1.0	0.001	3.00	3.0	3.0
2.0	0.002	2.71	Observed and calculated values agree from here down	
4.0	0.004	2.41		
6.0	0.006	2.23		
8.0	0.008	2.11		
2.0 cc. 0.5 <i>M</i>	0.01	2.01		
4.0	0.02	1.71		
6.0	0.03	1.55		
8.0	0.04	1.41		
9.0	0.045	1.37		
1.0 cc. 1.0 <i>M</i>	0.05	1.33		

¹ Cf. Sørensen, *Loc. cit.*

In his admirable work on the kinetics of invertase action, Hudson¹ obtained a value for the optimum of invertase action at $p_H^+ = 3.1$, whereas that obtained by Sørensen,² Michaelis and Davidsohn,³ and the present authors is in the neighborhood of $p_H^+ = 4.2$ to 4.4 . This difference of Hudson's is due very likely, in part at least, to the fact that Hudson calculated the concentrations of hydrogen ion from the molarity of the hydrochloric acid present. Such a calculation introduces more or less of an error when the actual index of the solution lies between 4.0 and 9.0 , as will be further seen upon examination of the following table, showing the calculated and the observed values in the case of dilute sodium hydroxide solutions.

TABLE VIII.

Cc. NaOH in 100 cc.	Molarity of NaOH.	Calc. values for p_H^+ .	Obs. values for p_H^+ . Ordinary distilled water.
0.1 cc. 0.01 <i>M</i>	0.00001	9.14	
0.2	0.00002	9.44	
0.3	0.00003	9.62	6.3 (<i>p</i> -nitrophenol)
0.4	0.00004	9.74	
0.5	0.00005	9.84	
0.6	0.00006	9.92	7.1 (rosolic acid)
0.7	0.00007	9.99	
0.8	0.00008	10.04	7.8 (rosolic acid)
0.9	0.00009	10.09	
1.0	0.0001	10.14	8.7 (phenolphthalein)

The above differences between the calculated and the observed values for p_H^+ firmly establish the necessity of actually measuring the concentration of hydrogen ion instead of just calculating it from the molarity of the acid or alkali used.

Measurement of Amount of Cane Sugar Inverted.

Owing to the fact that a concentration of cane sugar of 5 g. per liter was used in this work, it was not practicable to use the polariscope to measure the amount of inversion, nor to use any of the numerous sugar tables. Therefore, a modified Defren's method³ was used as follows:

Reagents.—34.64 g. of copper sulfate dissolved in water, 0.5 cc. conc. sulfuric acid added, and made up to 500 cc. 178 g. sodium potassium tartrate and 50 g. of sodium hydroxide dissolved in water and diluted to 500 cc.

Determination.—Mix 15 cc. of each of the above reagents in an Erlenmeyer flask having a capacity of 250 to 300 cc., dilute with 65 cc. of distilled water, then add 10 cc. of the sample undergoing hydrolysis, place in boiling water bath and allow to stand for exactly fifteen minutes. Remove the flask from the bath and filter at once (using moderate suction) through asbestos specially prepared as usual for this purpose; wash the cuprous

¹ THIS JOURNAL, 32, 1220 (1910).

² *Loc. cit.*

³ Cf. Defren, THIS JOURNAL, 18, 749 (1896).

oxide with boiling distilled water until free from alkali. Dissolve the cuprous oxide in 6 *M* nitric acid, etc., and determine the copper by means of potassium iodide and sodium thiosulfate. It is necessary to run a blank control to determine the correction to be applied for the effect of the Defren method on cane sugar itself. Under the conditions of our experiments we found the reducing effect of 50 mg. cane sugar to be equivalent to 2.8 mg. cupric oxide, or 1 mg. cane sugar inverted.

From the weight of cupric oxide corresponding to the weight of copper found, the amount of cane sugar inverted was calculated according to the following sugar table constructed by the authors as hereinafter described:

TABLE IX.

Mg. CuO.	Mg. cane sugar inverted.	Mg. CuO.	Mg. cane sugar inverted.
10	3.6	70	27.2
20	7.2	80	31.5
30	11.0	90	35.9
40	14.9	100	40.4
50	18.9	110	45.0
60	23.0	120	49.7

Construction of Sugar Table.

280 cc. of sugar solution containing 59.998 g. cane sugar were made up to 300 cc. with "stock solution" of invertase and 0.2 cc. 0.1 *M* hydrochloric acid, which brought the index of the solution down to 4.8. The flask containing this solution was placed in the thermostat, which was maintained at the usual temperature of $37^{\circ} \pm 0.01^{\circ} \text{C}$. A 50 cc. sample was withdrawn at 15, 30, 60, 120 and 180 minutes, respectively, and run into 16.7 cc. of 0.2 *M* sodium carbonate solution, as recommended by Hudson for arresting inversion and eliminating the effect due to mutarotation.

10 cc. or 20 cc. were withdrawn from this 66.7 cc. and diluted twenty or thirty times, and a Defren's determination, as already described, run on 10 cc. portions from the diluted solution. The rest of the 66.7 cc. was used to determine the amount of inversion by means of the polariscope in the first series of determinations, and by means of the saccharimeter in the second series.

TABLE X.

Conversion of Polariscope Readings to Percentage Inversion.

Time. Mins.	Readings at 30°.			Average.	Angle of inversion.	% Inversion
	21.90	(calc.)	...			
Start	21.90	(calc.)
15	20.36	20.40	...	20.38	1.52	5.52
30	18.83	18.86	18.86	18.85	3.05	11.08
60	16.13	16.15	16.14	16.14	5.76	20.96
120	11.15	11.18	11.21	11.18	10.72	38.94
180	7.38	7.36	7.36	7.37	14.53	52.78
	-5.63	(calc.)				

TABLE X (continued).

Conversion of Saccharimeter Readings (Ventzke) to Percentage Inversion.

Time. Mins.	Readings at 35°.		Average.	Angle of inversion.	% Inversion.
Start	62.8	62.8	62.8
15	58.6	58.6	58.6	4.2	5.41
30	55.0	55.0	55.0	7.8	10.04
60	48.2	48.2	48.2	14.6	18.80
120	35.2	35.2	35.2	27.6	35.53
180	24.2	24.2	24.2	38.6	49.69
240	14.5	14.5	14.5	48.3	62.18
2220	-14.3	-14.3	-14.3	77.1	99.26
	-14.6	(calc.)			

TABLE XI.

Determination of Amount of Cane Sugar Inverted Corresponding to Cupric Oxide.

Dilution of sample from 66.7 cc. ¹					Dilution of sample from 66.7 cc. ¹					
Dilution of sample from 66.7 cc. ¹		Equiv. grams cane sugar in 10 cc. used for Defren's.	Percentage inversion.	Grams CuO.	Dilution of sample from 66.7 cc. ¹		Equiv. grams cane sugar in 10 cc. used for Defren's.	Percentage inversion.	Grams CuO.	
10 cc. made up to	100	0.1499	5.52	0.0227	20 cc. made up to	600	0.0500	5.41	0.0085	
	200	0.0750	11.08	0.0230		600	0.0500	10.04	0.0155	
	250	0.0580	20.92	0.0328		600	0.0500	18.80	0.0254	
	200	0.0750	38.94	0.0748		600	0.0500	35.53	0.0456	
	200	0.0750	52.78	0.0982		600	0.0500	49.69	0.0633	
							600	0.0500	62.18	0.0795
							600	0.0500	99.26	0.1200

If these results are expressed in the form of an equation, derived by the method of least squares, we get

$$\text{Cane sugar inverted} = 0.351 W + 0.000527 W^2$$

where W is the weight of cupric oxide obtained, the values of W varying from 8 to 120 mg.

The values in the sugar table already given were calculated by the use of this equation.

The agreement between the values obtained by experiment and those calculated by the use of the above equation is shown in Table XII.

TABLE XII.

Mg. cane sugar inverted.		Diff.	Mg. cane sugar inverted.		Diff.
Mg. CuO.	Obs.		Mg. CuO.	Obs.	
8.5	2.7	3.0	45.6	17.8	17.1
15.5	5.0	5.7	63.3	24.8	24.3
22.7	8.3	8.3	74.8	29.2	29.2
23.0	8.3	8.4	79.5	31.1	31.2
25.4	9.4	9.2	98.2	39.6	39.5
32.8	12.1	12.1	120.0	49.6	49.6

Summary.

The concentration of hydrogen ion remains constant throughout the whole course of the inversion of cane sugar by means of invertase.

¹ Of these diluted solutions, 10 cc. were used for Defren's.

At the optimum of invertase action, the salt effect of the sodium chloride seems to approach zero, and as we depart either side from the optimum, we get an increasing salt effect.

The use of buffers (tampons) for regulating the concentration of hydrogen ion introduces a certain salt effect. The most satisfactory region for using buffers in invertase velocity measurements is in the neighborhood of the optimum zone where the salt effect is a minimum.

In the region of enzyme activity it is necessary to measure the concentration of hydrogen ion, and it is not permissible to calculate it from the molarity of acid used.

The addition of sodium chloride to solutions of hydrochloric acid causes an increase in the concentration of hydrogen ion as measured by the electromotive force method and by the hydrolysis of cane sugar solutions.

NEW YORK, N. Y.

CORRECTION.

The Dissociation of Carbon Oxydisulfide.—Through the kindness of Professor J. Sakurai, of the University of Tokio, my attention has been called to an important error in sign in the recent paper by Lewis and Lacey.¹ There it is stated, "It is evident that with diminishing temperature the equilibrium is shifted in favor of CO." This should have read "with increasing temperature." Consequently, the van't Hoff equation gives for the heat of formation of COS from liquid sulfur and carbon monoxide not -11000 but $+11000$ calories. For this reaction Berthelot found -4000 and Thomsen $+10000$ cal. Our value therefore corroborates that of Thomsen, and we may now feel safe in using this value in the calculation of the free energy of the reaction at standard temperature. This calculation will be made in another place. GILBERT N. LEWIS.

NEW BOOKS.

Laboratory Manual to Accompany "A Course in General Chemistry." By Wm. McPHERSON AND Wm. E. HENDERSON. Ohio State University. Pp. v + 142. Ginn and Co., 1915. Price, 60 cents.

The role this manual plays is well stated in the preface by the authors: "For one who sets about the task of arranging an experimental course for the beginner, there remains little opportunity for originality or invention. His problem is rather one of selection. Accordingly, this laboratory manual lays no claim to originality, either in method or in content." When used in connection with the text-book, by the same authors, it proves to be a fairly satisfactory guide for an elementary course. The introductory experiments are not well chosen. For example, the student infers from the experiment that when salt is dissolved in water the change

¹ THIS JOURNAL, 37, 1981 (1915).

is merely physical. Since the beginning student invariably uses an excess of acid, it is suggested in the preparation of zinc sulfate that the water bath be used in place of the sand bath, thus avoiding the disagreeable fumes of sulfur trioxide. Iron, sulfur and iron sulfide could be more completely identified in Experiment 11, by the use of suitable solvents. While large quantities of oxygen are isolated by a laboratory method in Exp. 15, no mention is made that this oxygen is to be used later in Exp. 18. More experiments to illustrate the chemical activity of oxygen should be given. The diagrams and the apparatus used in the isolation of hydrogen and oxygen can be improved. In the preparation of carbon monoxide, the generator should be provided with a safety tube or else an empty bottle should be inserted between the generator and the bottle containing sodium hydroxide. On the whole, the experiments are well selected and the manual serves the purpose for which it was intended.

LILLIAN COHEN.

Annual Reports of the Progress of Chemistry for 1915. Issued by the Chemical Society of London. Vol. XI. New York: D. Van Nostrand Co., 1915. 15 X 21 cm. Pp. viii + 303. Cloth: Price, \$2.00 net.

The subject matter of this volume has been divided under the following headings: General and Physical Chemistry, Inorganic Chemistry, Analytical Chemistry, Physiological Chemistry, Agricultural Chemistry and Vegetable Physiology, Mineralogical Chemistry, and Radioactivity. In each case the reviewers have endeavored to select the important articles which have appeared during the year, devoting a reasonable amount of space to the presentation and discussion of their principal points of merit. This has resulted in the omission of a goodly number of articles from the report, some of which other reviewers might have included. On the whole, the volume must be pronounced a decided success. The work has been done thoroughly and courageously, for it certainly does require courage to go ahead and select from a large mass of material that which seems important and worthy of special mention.

The work done during the year on the structure of atoms, the mechanism of electrical conduction, the atomic weight of lead as bearing on the question whether atomic weights may change or not, the researches on sugars, improvements in methods of gas analysis and water analysis, enzymes, vitamins, the study of crystals by X-ray methods, liquid crystals and radioactivity is especially well presented. The reviewer has read the volume with interest. No article of special importance seems to have been omitted in this summary for the year. The work of the authors is highly commendable.

LOUIS KAHLENBERG.

Brief Course in Metallurgical Analysis. By HENRY ZIEGLER. Easton, Pa.: The Chemical Publishing Co. 1915. Pp. vi + 72. Price, \$1.00.

The author states that the "book is written for the use of upperclass-

men," the work to require ten to twelve hours per week for two semesters, and to include "standard analyses in daily use in various analytical laboratories." The analytical procedures include those for iron ores, iron and steel, limestones, slags, clays, non-ferrous alloys, and some non-ferrous ores. A bibliography is appended.

The book contains so many imperfections in proof-reading, composition and chemistry that it is difficult to see how it can fulfil a useful purpose.

H. P. TALBOT.

Anesthesia. BY JAMES TAYLOR GWATHMEY, in collaboration with CHARLES BASKERVILLE. With 283 illustrations in the text. D. Appleton and Company, New York and London. 1914. xxxiii + 945 pp.

Dr. Gwathmey and Professor Baskerville have been assisted in the preparation of the volume by the following investigators, who have contributed individual chapters: W. B. Gatch, Walter S. Sutton, James F. Mitchell, Hermann Prinz, Louise G. Robinovitch, James J. Walsh, H. W. Frink and John W. H. Crim.

The main purposes of the book as set forth by the authors are:

1. To give in a practical and utilizable form the essentials of the subject of the administration of anesthetics.
2. To save the busy medical practitioner or student the labor of weeding out from the voluminous literature upon the subject the facts which he must constantly bear in mind in the successful practice of this important branch of medicine.
3. To emphasize, wherever possible, the thought that "to bring a living being to that borderland in which life in many respects so simulates death should at no time be a fool's occupation;" and
4. While primarily intended as a work for the active practitioner and student, to suggest many lines for further research.

An important feature of the book is the discussion of the chemistry of anesthetics. "As modern medicine now more fully recognizes the importance of a knowledge of chemistry in all of its branches, that phase of the subject has been quite fully developed, not only along lines of original purity of the drug used, the conditions favorable to its preservation in its highest purity, but its course within the body, resulting either in the destruction of the drug or its elimination from the body."

Over one hundred and fifty pages are devoted to a very complete list of anesthetics with important data and references pertaining to the same. This feature of the book should appeal to the chemist as well as physician.

The volume is thoroughly up-to-date in every respect and impresses the reviewer as the most acceptable treatise on anesthesia which has yet appeared.

PHILIP B. HAWK.

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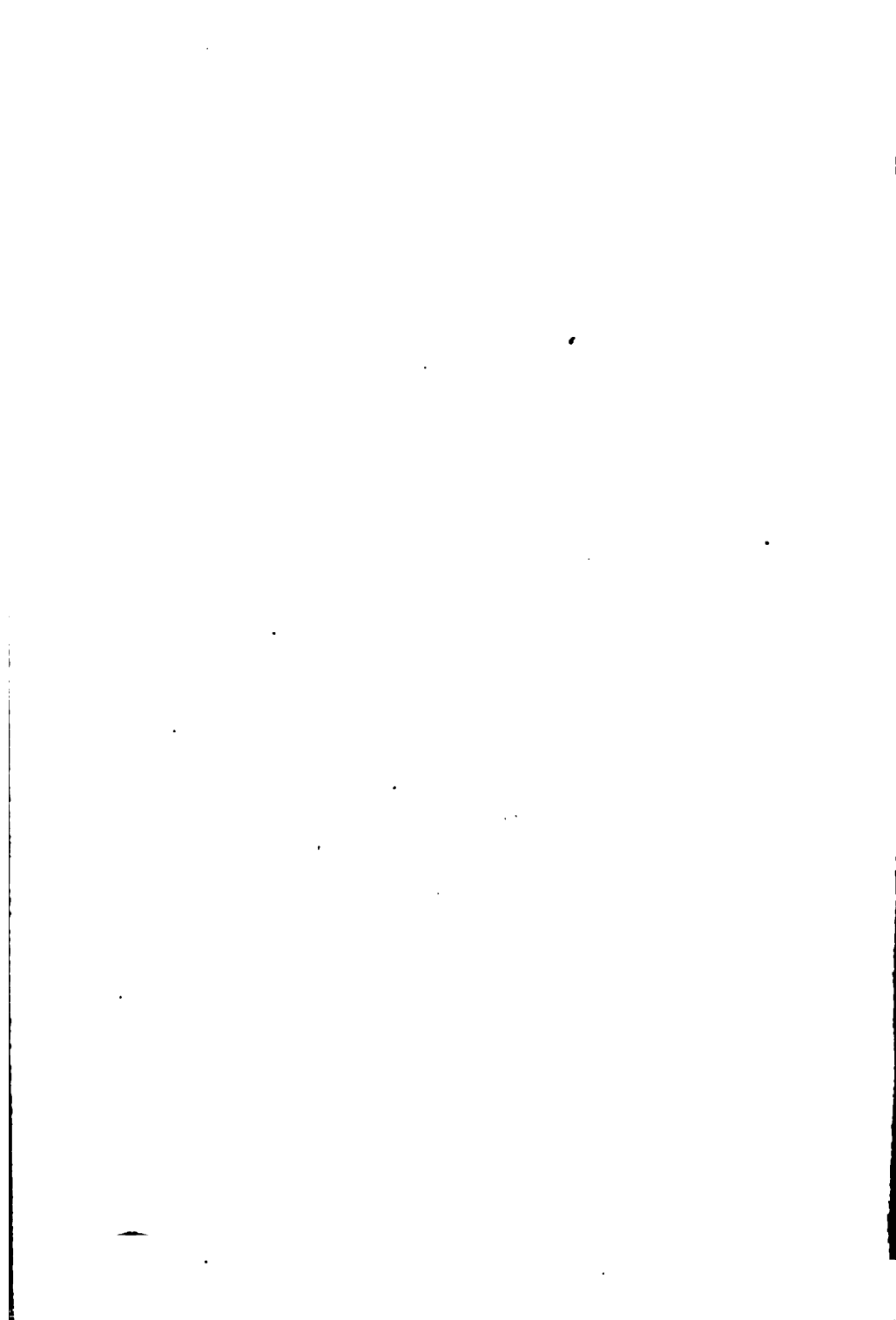
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GENERAL SOCIETY MINUTES AND REPORTS.

On November 1st, a nominating ballot was sent to all members of the Society as required by the Constitution, the following being the nominees of the membership sent to the Council for election:

President: C. H. Herty, Wm. Brady, Louis Kahlenberg and L. H. Baekeland.

Councilors-at-Large: E. C. Franklin, G. B. Frankforter, F. K. Cameron, L. W. Jones, A. L. Day, C. L. Alsberg, David Wesson, G. A. Hulett.

The ballot was counted by a committee consisting of C. L. Parsons, W. D. Bigelow and S. C. Brinton, assisted by seven other members of the Society.

The result of the election by the Council will be found in the Council minutes.

Report of the Secretary of the American Chemical Society for the Year 1914.

The growth of the American Chemical Society during the year 1914 has increased slightly over that of 1913. The Society has made a net gain of 497 members during the year. The membership of the Society at the end of 1913 was 6673. It is now 7170. Statistics follow:

Honorary members.....	14
Life members.....	13
Corporation members.....	63
Members.....	7,080
Total.....	7,170

During the year the deaths of the following members were reported to the Secretary: Ethel E. Barnard, Chicago, Ill.; D. W. Chapman, Chicago, Ill.; G. F. Chatfield, Lawrenceville, Ill.; A. C. Claudet, London, Eng.; H. D. Crumley, Boston, Mass.; W. L. Dudley, Nashville, Tenn.; Robert K. Duncan, Pittsburgh, Pa.; Arthur Edgar, Whitehaven, Pa.; Herman Frasch, New York City; M. S. Fremont, Astabula, O.; Louis D. Gilbert, Santa Rosa, Calif.; Thos. J. Hunsicker, Lebanon, Pa.; W. K. Jewett, Lincoln, Nebr.; Eugene McSweeney, Saginaw, Mich.; Johnson Newkirk, Ridley Park, Pa.; Russell Penniman, Berkeley, Calif.; E. H. Rankin, Bayonne, N. J.; Andrew Robertson; C. H. Senff (Life Member), Whitestone, N. Y.; J. S. Stillwell, West Orange, N. J.; J. C. H. Stut, Oakland, Calif.; B. F. Thomas, Chattanooga, Tenn.; A. P. Trautwein, Carbondale, Pa.; H. F. Walker, Lewiston, Pa.

The number of members not in arrears registered in the Local Sections

on December 1, 1913 was 5,069; the number on December 1, 1914 was 5,414. The number in each Section for 1913 and 1914 is noted below:

Local section.	Number of paid mem- bers, 1913.	Number of paid mem- bers, 1914.	Cash retained from balance, 1913.	Total Dr account, 1914.
Alabama.....	31	33	13.85	13.85
California.....	174	179	...	165.00
Chicago.....	437	486	...	327.75
Cincinnati.....	102	115	64.64	127.50
Cleveland.....	166	166	43.87	166.00
Columbus.....	47	69	14.80	70.50
Connecticut Valley.....	62	68	...	75.00
Cornell.....	52	42	15.60	65.60
Detroit.....	64	71	...	80.00
Eastern New York.....	63	58	33.78	58.78
Georgia.....	59	57	...	67.99
Indiana.....	100	101	...	123.75
Iowa.....	52	54	9.50	59.50
Kansas City.....	80	80	4.75	100.00
Lehigh Valley.....	59	64	20.72	20.72
Lexington.....	25	21	13.12	13.12
Louisiana.....	35	31	1.00	52.50
Louisville.....	18	15
Maine.....	41	47	...	25.00
Maryland.....	..	78
Milwaukee.....	52	63	...	75.00
Minnesota.....	83	82	39.34	39.34
Nashville.....	21	21	10.08	35.08
Nebraska.....	29	27	32.40	50.00
New Haven.....	58	57	...	75.00
New York.....	1,006	1,057	23.26	323.26
North Carolina.....	38	36	19.85	69.85
Northeastern.....	478	507	1.50	251.50
Northern-Intermountain.....	16	20
Oregon.....	29	28	15.45	50.00
Philadelphia.....	297	307	27.19	222.75
Pittsburgh.....	230	258	8.24	172.50
Puget Sound.....	45	44	...	50.00
Rhode Island.....	57	65	10.59	60.59
Rochester.....	38	31	...	50.00
St. Louis.....	83	91	...	103.75
Southern California.....	84	97	...	100.00
South Carolina.....	28	25	...	25.00
Syracuse.....	77	95	24.90	96.25
University of Illinois.....	88	109	1.75	101.75
University of Michigan.....	35	38	33.66	33.66
University of Missouri.....	18	15	5.66	30.66
Washington, D. C.....	365	327	...	273.75
Western New York.....	91	104	...	113.75
Wisconsin.....	84	86	32.30	32.30
	5,069	5,419	\$521.80	\$4,248.30

The table gives a summary of the sectional accounts for the year, shows the number of members in each Section for the present year and during 1913, the funds held over from 1913 account, and the total funds (which include the balances) charged to the 1914 account.

During the past two fiscal years, December 1, 1912, to December 1, 1914, the Secretary has made collections to the amount of \$71,825.89, in 1913 and 76,805.97 in 1914 as follows:

	1913.	1914.
Membership dues.....	\$62,158.00	\$65,953.00
Subscriptions.....	4,998.00	5,761.59
Back numbers.....	2,417.95	2,514.07
Postage.....	951.09	1,054.13
Reprints.....	681.85	930.10
Exchange.....	19.79	19.44
Interest.....	399.21	373.64
Life membership.....	200.00	200.00
	<hr/>	<hr/>
	\$71,825.89	\$76,805.97

These amounts were duly transmitted to the Treasurer of the Society.

The sale of back numbers during the past year has again increased although it was expected that they would diminish. This is due to the fact that efforts have been made to induce libraries to purchase complete sets, and owing to the fact that the subscription list is continually enlarging, and purchasers desire early numbers as well.

Several complete sets have been sold to foreign and domestic libraries and several incomplete sets have been completed by the purchase of odd volumes where they could not be furnished from stock. The stock has been kept in good condition by the purchase of numbers needed to complete full volumes and by reprinting three small numbers issued in the early years of the Society. A few complete sets are still available for sale.

Back numbers are mailed direct from Easton, Pennsylvania, on orders sent out through the Secretary's Office. The following is a summary of the back numbers sent out by the Secretary during the year, together with the present stock of Journals and the condition of the Society's mailing lists:

Copies of the Society's publications sent out from December 1, 1913, to December 1, 1914, aside from mailing lists.....	27,921
Copies of the <i>Jour. Amer. Chem. Soc.</i> in stock.....	28,443
Copies of the <i>Chemical Abstracts</i> in stock.....	23,986
Copies of the <i>Jour. Ind. & Eng. Chem.</i> in stock.....	7,173
Copies of the General Index, Vols. 1-20, <i>J. A. C. S.</i> in stock....	448
Copies of the Anniversary Number in stock.....	277
Mailing list for both Journals and <i>Chemical Abstracts</i>	6,543
Mailing list for <i>Chemical Abstracts</i> only.....	194
Mailing list for <i>Jour. Amer. Chem. Soc.</i> only.....	393
Mailing list for <i>Jour. Ind. & Eng. Chem.</i> only.....	407

The Secretary wishes to express to the members of the Society his appreciation for their continued assistance and loyal support of his efforts to administer the duties of his office. Without this aid little could have been accomplished. Respectfully submitted,

CHARLES L. PARSONS, *Secretary*.

Report of the Editor of the Journal of the American Chemical Society for the Year 1914.

During the years 1913 and 1914 papers and book reviews have been published as follows:

	Pages.		Number of papers.	
	1913.	1914.	1913.	1914.
Proceedings.....	114	112
Physical and Inorganic.....	1029	1154	107	115
Organic and Biological.....	818	1320	111	136
Book Reviews.....	75	80	85	93

During the past year eleven papers have been referred to the Editor of the *Journal of Industrial and Engineering Chemistry* as more suitable for publication in that Journal than in the *Journal of the American Chemical Society*. Forty-four papers have been returned to the authors for revision, or because they were not considered suitable for publication. Twenty-three papers have been published after revisions made at the suggestion of the Board of Editors.

Beginning with January of 1914 the *American Chemical Journal* has been incorporated with the *Journal of the American Chemical Society* as a single publication. The number of pages published in the combined journal during the year is about 33% greater than the number of pages published during 1913.

W. A. NOYES, *Editor*.

Report of the Editor of Chemical Abstracts for 1914.

The year that has just closed has been an eventful one for Chemical Abstracts in that The European War came upon us about the middle of this period. At first we thought its effect would be slight and that it would not seriously affect the bulk of chemical literature or the volume of abstracts, but such has not been the case. From January to September the issues of C. A. were unusually large, but subsequent to the interruption of international trade relations the number of abstracts received has been comparatively small. This latter condition accounts for the fact that the number of abstracts printed in 1914 is slightly less than for 1913.

Among the changes in personnel of the editorial staff is the resignation of Dr. Patterson from the editorship of Chemical Abstracts. In his retirement, which was solely because of ill health, the Society lost a very loyal and efficient editor and one to whom it will always owe a debt of gratitude for the sound judgment which he exercised in moulding the policy of Chemical Abstracts.

Other editorial changes consist in the installation of Drs. M. X. Sullivan and R. T. Stokes as Heads, respectively, of the Departments of Soils and Fertilizers and Rubber and Allied Products. For the long and faithful services of Drs. F. P. Veitch and D. Spence as Editors of these departments the Society is greatly indebted.

It may be well to call attention to the fact that the List of Periodicals abstracted by Chemical Abstracts was printed in the September 10th issue. Whereas in 1913 the journals abstracted numbered 623, this year 654 have been covered completely. We hope that it will not be necessary to increase this number for several years to come and trust that such will be the case, because there are probably no chemical journals of consequence in the entire world which are not now upon our List.

Below is a table showing the average length of the abstracts (both patent and otherwise) for 1914 in comparison with the figures for previous years.

Year.	Pages (blanks omitted).	No. of abstracts.	Length of abstracts.	Pages patents.	No. of patents.	Length of patents.
1907.....	2584.4	7,975	0.324	462.0	not	...
1908.....	2928.5	10,835	0.270	355.3	ctd.	...
1909.....	2565.3	11,455	0.224	365.8	3806	0.096
1910.....	2894.9	13,006	0.223	387.0	3754	0.103
1911.....	3260.3	15,892	0.205	542.8	5014	0.108
1912.....	2888.6	15,740	0.183	537.5	6919	0.077
1913.....	3292.5	19,025	0.173	576.4	6946	0.083
1914.....	2966.8	16,468	0.180	661.4	7920	0.084

It is evident from the above data that the standard length set for 1912 (0.183 page) and 1913 (0.173 page) has been approximately maintained. In explanation we should say however, that it was necessary to make the abstracts so brief in order to avoid overrunning our Budget allowance. It is our hope during 1915 to be able to expand the abstracts somewhat and to allow the abstractors more freedom of expression. The average length of the patent abstracts has been almost identical with that of 1913, but the number of such abstracts has increased somewhat because during 1914, for the first time in the history of our journal, all of the patent literature of the world has been abstracted.

The summary by departments is as follows:

	No. pages.	No. abstracts.
Apparatus.....	38.8	333
General and Physical Chemistry.....	305.0	1658
Radioactivity.....	66.6	324
Electrochemistry.....	66.5	425
Photography.....	11.5	81
Inorganic Chemistry.....	87.4	366
Analytical Chemistry.....	75.5	370
Mineralogical and Geological Chemistry.....	73.2	575
Metallurgy and Metallography.....	89.2	699
Organic Chemistry.....	683.9	1510

	No. pages.	No. abstracts.
Biological Chemistry.....	706.8	4692
Foods.....	80.1	506
Water, Sewage and Sanitation.....	54.1	516
Soils and Fertilizers.....	72.2	555
Fermented and Distilled Liquors.....	36.2	248
Pharmaceutical Chemistry.....	99.7	714
Acids, Alkalies, Salts and Sundries.....	17.1	172
Glass and Ceramics.....	53.3	395
Cement and Other Building Materials.....	32.9	212
Fuels, Gas, Tar and Coke.....	51.9	413
Petroleum, Asphalt and Wood Products.....	32.4	217
Cellulose and Paper.....	25.8	194
Explosives.....	32.3	177
Dyes and Textile Chemistry.....	36.3	204
Pigments, Resins, Varnishes and Rubber.....	40.6	263
Fats, Fatty Oils and Soaps.....	29.4	207
Sugar, Starch and Gums.....	45.8	284
Leather and Glue.....	22.2	158
<hr/>		
Total, not including patents.....	2,966.8	16,468
Patents.....	661.4	7,920
<hr/>		
	3,628.2	24,388
Headings, blanks, cross references, book titles..	243.8	
<hr/>		
	3,872.0	

Respectfully submitted,

JOHN J. MILLER, *Editor*.

Report of the Editor of the Journal of Industrial and Engineering Chemistry for the Year 1914.

We have produced during the past year 89,000 copies of the *Industrial Journal*. The printing has been divided as follows: 1066 pages of editorial matter equivalent to 88½ pages per month, and 702 pages of advertising matter equivalent to 58½ pages per month. The editorial matter, together with a comparison of this work in previous years, may be summarized as follows:

	1911.	1912.	1913.	1914.
Pages in editorial section.....	970	946	1052	1066
Pages in advertising section.....	158	494	604	702
Total pages printed.....	1128	1440	1656	1768
Editorials.....	30	19	28	21
Original papers.....	140	160	179	187
Addresses.....	22	37	57	57
Laboratory and Plant articles.....	28	55	43	40
Book Reviews.....	36	53	52	72
Patents.....	172	206
Current Industrial News items.....	136

The additional material for the 1914 volume is made up of Scientific Society reports, notes and correspondence, abstracts from Government reports, personals and general matter.

The column on Government Publications has been added during the last year, and our policy has been endorsed by numerous letters received in this office. We believe it is a distinct advantage to be able to find an up-to-date summary of all of the publications of the Government which might be of professional interest. Respectfully submitted,

M. C. WHITAKER.

Treasurer's Report Dec. 1913 to Dec. 1, 1914.

SUBJECT TO AUDIT.

Balance on hand, Dec. 1, 1913..... \$8,314.98

RECEIPTS.

	1913. ¹	1914.
From Secretary's office.....	\$71,825.89	\$76,805.97
From advertising.....	19,901.51	25,056.06
From interest:		
Farmer's Loan & Trust Co.....	96.65	163.33
Certificates of deposit.....	300.00	343.21
1st National Bank of Yonkers.....	24.59	108.25
From interest on investments:		
Atlas Portland Cement Bonds.....	120.00	120.00
Other bonds.....	90.00
From interest on special funds:		
Special investment funds.....	570.00	570.00
Life membership fund.....	135.00	145.82
		\$103,402.64
Total receipts.....	\$92,973.64	\$103,402.64
		111,717.62
Disbursements.....		104,126.37

Balance on hand, Dec. 1, 1914..... \$7,591.25

LIST OF BONDS PURCHASED, \$5000 EACH ISSUE FOR THE LOEB FUND AND \$1000 FOR REGULAR FUND.

- \$6000. Brooklyn Rapid Transit Co. Six Year 5% Gold Notes due July 1, 1918, ex-July 1, 1914 coupon.
- \$6000. Northern Pacific-Great Northern C. B. & Q. Collateral Joint 4% Bonds due July 1, 1921, ex-July 1, 1914 coupon.
- \$6000. Hocking Valley Railway Co. First Consolidated Mtge. 4 $\frac{1}{2}$ % Gold Bonds due July 1, 1999, ex-July 1, 1914 coupon.
- \$6000. New York Connecting Railroad Company First Mtge. 4 $\frac{1}{2}$ % Gold Bonds due August, 1953.
- \$6000. Illinois Central Railroad Co. & Chicago, St. Louis & New Orleans Railroad Co. Joint First Refunding Mtge. 5% Bonds, due December, 1963.

ASSETS.

Special Investment Fund:

\$2000 3 $\frac{1}{2}$ % N. Y. City gold bonds, due 1915.....	\$1,950.00
\$10,000 U. S. Steel Corp. gold bonds, 1963.....	10,075.00
	<u>\$12,025.00</u>

¹ 1913 figures are given for comparison.

Atlas Portland Cement Co. bonds 6%.....	2,040.00
Brooklyn Rapid Transit Co. 6 year 5% gold notes.....	
Northern Pacific-Great Northern C. B. & Q. 4% bonds.....	
Hocking Valley Railway First Consolidated Mtge. 4 1/2% gold bonds...	5,184.46
N. Y. Connecting Railroad Co. First Mtge. 4 1/2% gold bonds.....	
Illinois Central Railroad Co. & Chicago, St. Louis & New Orleans Railroad Co. Joint 1st Mtge. Refunding Mtge. 5% bonds.....	

Life Membership Fund:

\$1,000, 3 1/2% N. Y. City gold bonds due 1928.....	895.00	
\$2,000, 6% Mutual Telegraph Co. bonds due 1941.....	2,128.33	
Emigrant Savings Bank.....	628.82	\$3,652.15

Balance on hand.....	7,591.75
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\$30,492.86

LIABILITIES.

Life Membership Fund.....	628.82
Excess assets over liabilities.....	29,864.04

\$30,492.86

MORRIS LOEB FUND.

Balance from last year.....	\$25,000.00
Received from interest.....	1,037.35

\$26,037.35

Paid for bonds.....	25,276.52
Chemists' Club.....	700.00

\$25,976.52

Balance on hand.....	\$60.83
----------------------	---------

DISBURSEMENTS.

	1913. ¹	1914.
<i>Journal</i> , Editor's salary.....	\$1,000.00	\$1,000.00
Assistance to Editor.....	237.00	360.00
Expense.....	129.09	129.86
Printing, Editorial.....	9,034.35	13,410.48
Printing, Advertisements.....	334.59	367.89
Reprints.....	731.03	936.35
Reviews.....	34.00
	\$11,466.06	\$16,238.58
<i>Abstracts</i> , Editor's salary.....	\$500.00	\$1,062.45
First Associate Editor.....	1,700.00	1,904.11
Second Associate Editor.....	1,200.00	933.28
Assistance to Editor.....	2,232.99	2,520.64
Expense.....	628.78	668.96
Abstractors.....	8,147.22	8,448.41
Printing, Editorial.....	22,381.32	23,573.04
Printing, Advertisements.....	468.33	472.70
	\$37,258.64	\$39,583.99

¹ 1913 figures are given for comparison.

<i>Jour. Ind. & Eng. Chem.</i> , Editor's salary . . .	\$1,000.00	\$1,000.00
Assistant Editor.....	1,337.50	1,533.33
Expense.....	952.34	954.85
Clerical.....	1,032.00	1,156.00
Reprints.....	1,489.42	1,221.87
Printing, Editorial.....	11,318.26	11,211.27
Printing, Advertisements.....	4,704.10	5,355.94
	<hr/>	<hr/>
	\$21,833.62	\$22,433.26
Advertising, Commission.....	\$3,635.03	6,339.27
Expense.....	513.15	24.06
	<hr/>	
Secretary's Office, Clerical.....	\$2,218.32	2,548.23
Expense.....	1,532.69	1,748.60
Commission.....	3,591.29	3,500.00
	<hr/>	
Treasurer's Office, Salary.....	300.00	300.00
Expense.....	400.00	400.00
General Meetings.....	654.51	385.60
Local Sections.....	3,406.31	3,726.50
Back Numbers.....	689.37	830.63
Incidentals.....	308.69	353.17
President's Office.....	50.07
Directory.....	480.32
Bond Investment.....	5,184.46
Committee on Business Organization.....	232.10
	<hr/>	<hr/>
Total Disbursements.....	\$88,480.87	\$104,126.37

DIRECTORS' MINUTES.

The Directors met at the Chemists' Club, New York City, Saturday, December 5, 1914, at 8 P.M., with President Richards in the Chair and Directors Bigelow, Bogert, Brady, Hallock, Love, Smith, and Parsons present.

It was voted that the Seattle Meeting of the American Chemical Society be held August 31 to September 3, 1915.

It was voted that a sum not exceeding \$25 be paid to the Maryland Section of the American Chemical Society to cover their necessary expenses (as provided by the Constitution) since they became a separate section of the Society.

It was voted that a special concession in subscription rates of \$3.00 per year for the *Journal of the American Chemical Society* and \$3.00 per year for the *Journal of Industrial and Engineering Chemistry* be made to undergraduate students in chemistry when their request for such subscription is accompanied by the certification of the professor in charge of their work that they are entitled to same. This concession to undergraduate students is made in the hope that it may lead them to actively assist in the work

of the American Chemical Society as members after graduation. It in no way effects the privileges they now possess of becoming members of the American Chemical Society when properly recommended.

It was voted that Mr. E. J. Crane be made Acting Editor of *Chemical Abstracts* to fill the vacancy made by the resignation of Mr. J. J. Miller. It was voted that the salary of Mr. E. J. Crane as Acting Editor be \$1800 per annum, beginning January 1, 1915. It was voted that Messrs. J. J. Miller and E. J. Crane be allowed to select, subject to the approval of the President and the Secretary, an Associate Editor of *Chemical Abstracts*, the salary of such Associate Editor not to exceed \$1200 if inexperienced, and not to exceed \$1500 if an experienced man can be found.

It was voted that the Finance Committee be authorized to invest in bonds, subject to the approval of the President, Five Thousand Dollars (\$5000) from the general funds of the Society.

It was voted that a committee consisting of Directors Alexander Smith, Chairman, and M. T. Bogert and E. G. Love be appointed from the Directors to consult with the Trustees of the Chemists' Club regarding the character and form of the Chemical Type Museum to be founded under the bequest of Dr. Morris Loeb, and report as to the disposition of the funds paid to the Club by the American Chemical Society from this bequest.

It was voted to transfer \$100 from the Incidentals Account to the Secretary's Clerical and Expense Account.

It was voted that the Finance Committee, acting with the consent of the President, be authorized to make temporary loans of the General Funds of the Society to such fiduciary institutions as may be approved by them.

The Budget for 1915 was then considered by the Directors and adopted as follows:

BUDGET FOR 1915.

With 1914 Included for Comparison.

ESTIMATED RECEIPTS.

	1914.	1915.
Secretary's Office.....	\$72,000	\$76,000
Advertisements.....	20,000	24,000
Interest.....	1,000	1,200
Total.....	\$93,000	\$101,200

ESTIMATED EXPENDITURES.

Journal American Chemical Society:

Editor's salary.....	\$1,000	\$1,000
Expenses, including reviews.....	600	600
Printing, including reprints.....	14,400	15,400
Total.....	\$16,000	\$17,000

Category	1934	1935
Editor's salary	\$3,000	\$3,000
Acting Editor's salary	2,000	2,000
First Asst. Editor's salary	1,440	1,440
Clerical assistance	2,880	2,880
Expenses	600	600
Contractors and department heads	\$1,450	\$1,450
Printing, including index	24,800	24,800
Total	\$40,070	\$40,120
Industrial and Engineering Chemistry:		
Editor's salary	\$1,000	\$1,000
Acting editor's salary	2,500	2,500
First Asst. Editor's salary	1,836	1,836
Clerical assistance	11,500	11,500
Expenses	6,600	6,600
Contractors and department heads	\$23,526	\$23,526
Printing, including index	\$5,000	\$5,000
Total	\$40,962	\$40,962

Walker, Geo. T., 427 N. 14th St., East St. Louis, Ill.
 Werner, Emanuel F., 1402 A., North Kingshighway, St. Louis, Mo.
 Williams, Arthur G., 250 Grand River Ave., East Lansing, Mich.
 Williamson, Erskine D., Geophysical Lab'y, Washington, D. C.
 Wilson, Robert F., 55 N. Valley St., Akron, Ohio.
 Yost, Earl E., 639 N. Scott St., So. Bend, Ind.
 Young, Kwang P., 714 Conklin Pl., Madison, Wisc.
 Young, Yungyen, 135 University Station, Urbana, Ill.
 Zieman, Wm. W., 412 Daniel St., Champaign, Ill.

MEETINGS OF THE SECTIONS.

Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 503, Washington, D. C.]

WISCONSIN SECTION.

The December meeting was held in Madison, Wednesday, December 16th. The program was as follows: "Forms of Sulfur in Plant Materials and their Variations with the Soil Supply," by W. H. Peterson; "Some Phenomena of Tissue Self-digestion or Autolysis," by H. C. Bradley.

A. E. KOENIG, *Secretary*.

NEW YORK SECTION.

The regular meeting was held December 11th in conjunction with the New York Section of the Society of Chemical Industry and the American Electrochemical Society. The program was as follows: "A Surficial Burn Produced by an Unknown Radiation," by C. A. Doremus; "Past, Present, and Future of Electrochemistry in America," by E. F. Roeber; "Education for Chemical Research," by W. H. Walker; "Industrial Research in the Mellon Institute (illustrated)," by R. F. Bacon.

C. M. JONES, *Secretary*.

CONNECTICUT VALLEY SECTION.

The twenty-eighth meeting was held at Springfield, Mass., December 12th. The program was as follows: "Progress in the Hydrogenation of Oils," by Carleton Ellis.

J. C. ANDREWS, *Secretary*.

NEW HAVEN SECTION.

The December meeting was held Friday, the 4th. A lecture with demonstrations on "The Thermite Process of the Goldschmidt Thermite Company," was given by W. R. Hurlbert.

GEORGE S. JAMISON, *Secretary*.

LOUISIANA SECTION.

The eightieth meeting was held Friday, November 20th. The program was as follows: "Vanilla Extract Prepared by the Hot Percolation Process," by F. W. Liepsner; "A Criticism of Some Selected Analytical Methods," by Chas. S. Williamson, Jr.

J. HEATH LEWIS, *Secretary*.

DETROIT SECTION.

The November meeting was held Friday, November 27th. The pro-

gram was as follows: "Chemical Industries in Japan (illustrated)," by Jokichi Takamine.

The December meeting was held Friday, December 18th. The program was as follows: "The Bleaching of Shellac," by C. T. Bragg; "The Manufacture of Chemical Porcelain in Detroit," by Harry Spurrier; "The Manufacture of Insulated Wire," by Jas. H. Bogart; "Comparison of the Pharmacopoeiae of Different Countries," by H. T. Graber; "Some Features of the Gas Industry," by Leigh E. Worthing.

EDW. J. GUTSCHER, *Secretary*.

CORNELL SECTION.

The regular meeting was held Monday, December 14th. The program was as follows: "X-Ray Spectra of the Elements, the Periodic Law, and Theories of the Structure of the Atom," by G. B. Upton.

O. R. OVERMAN, *Secretary*.

UNIVERSITY OF ILLINOIS.

The December meeting was held Monday, December 14th. The subject of the evening was "Household Chemistry," and the speakers, Professors Isabel Bevier and N. E. Goldthwaite and Dr. Ruth Wheeler.

GEO. D. BRAL, *Secretary*.

PHILADELPHIA SECTION.

A joint meeting of the Engineers' Club and this section was held Saturday, December 5th. The address of the evening was on "The Bureau of Standards and Its Relations to the Industries," by F. W. Stratton, Director of Bureau of Standards, Washington, D. C.

The regular meeting was held Thursday, December 17th, and the address of the evening was on, "The Chemical Investigation of the Cause and Prevention of Dental Caries," by William J. Gies, Professor of Biological Chemistry, Columbia University.

C. S. BRIDGTON, *Secretary*.

ROCHESTER SECTION.

The Rochester Section accepted the hospitality of the University of Rochester on Monday evening, November 30th, when a lecture was given on "The Manufacture of Portland Cement," by Howard Rhode, of the Lehigh Portland Cement Co.

The regular meeting was held Monday, December 7th, the address of the evening was on "Paint Technology," by Henry A. Gardner, of the Institute of Industrial Research, Washington, D. C.

H. H. TOSMER, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The November meeting was held Tuesday, November 24th. The paper of the evening was on "Some Para-Hydroxytriphenylmethane Derivatives, a Contribution to the Chemistry of Free Radicals," by R. L. Jickling. The officers to serve for 1915 were elected as follows: *Chairman*, L. H. Cone; *Sec.-Treas.*, H. H. Willard; *Councilor*, S. L. Bigelow.

The December meeting was held Tuesday, December 8th. An address was given on "Ferments from Microscopical Fungi and their Practical Applications," by J. Takamine, of New York City.

H. H. WILLARD, *Secretary*.

OREGON SECTION.

The annual meeting was held in Portland, Saturday, November 28th. The program was as follows: "Modern Methods of Testing Auriferous Gravel Deposits," by A. S. Wells.

F. A. OLIMSTED, *Secretary*.

CALIFORNIA SECTION.

The eighty-second regular meeting was held in San Francisco, Saturday, December 5th. The paper of the evening was on "The Passivity of Iron," by S. W. Young, Stanford University.

BRYANT S. DRAKE, *Secretary*.

WASHINGTON SECTION.

The following officers were elected to serve for 1915 at the November 12th meeting: *President*, C. L. Alsberg; *First Vice-President*, R. B. Sosman; *Second Vice-President*, H. M. Loomis; *Secretary*, E. C. McKelvy; *Treasurer*, F. P. Dewey; *Council*, J. A. LeClerc, P. H. Walker, J. Johnston, F. P. Dunnington; *Executive Committee*, E. W. Boughton, A. N. Finn, R. C. Wells, O. F. Black.

The two hundred and forty-third meeting was held Thursday, December 10th. The program was as follows: "The Recovery of Osmiridium in the Electrolytic Refining of Gold," by F. P. Dewey, Bureau of the Mint; "The Presence of Primary Cleavage Products of Protein in Soils," by E. H. Walters, Bureau of Soils; "The Excretion of Thymol in the Urine," by A. Seidell, Hygienic Laboratory.

ROBERT B. SOSMAN, *Secretary*.

IOWA SECTION.

The December meeting was held Saturday, December 12th. The program of the evening was as follows: "Radio-Activity of Waters," by Herman Schlundt, of the University of Missouri; "Purification of Water," by L. H. Goebel, of the Cedar Rapids Water Works.

P. A. BOND, *Secretary*.

MARYLAND SECTION.

The third regular meeting was held Saturday, December 19th. The program was as follows: "Reminiscences of Liebig and Wohler," by In Remsen.

FRANK M. BOYLER, *Secretary*.

LEXINGTON SECTION.

The regular meeting was held Wednesday, December 9th. The program was as follows: "Report on the Annual Convention of the Association of Official Agricultural Chemists at Washington, November 16," by Wm. Rhodes; "Review: the Obtainment of Radium D in Visible Quantity and Its Identity with Lead," by A. M. Peter.

G. D. BUCKNER, *Secretary*.

CINCINNATI SECTION.

The one hundred and ninety-fourth regular meeting was held Wednesday, December 9th. The program was as follows: "Chemical and Physical Tests in the Manufacture of Paints," by P. Smyth; "Ice Cream Studies in Cincinnati," by C. Bahlmann; H. S. Fry read the following papers: "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences,—" Part 3; "A Continuation of the Interpretation of the Crum Brown and Gibson Rule,—" Part 4; "The Simultaneous Formation of Ortho-, Meta-, and Para-Substituted Derivatives of Benzene,—" Part 5: "A Reply to A. F. Holleman."

STEPHEN J. HAUSER, *Secretary*.

RHODE ISLAND SECTION.

The December meeting was held Thursday, December 17th. The program was as follows: "Abrasives," by James G. Callan of Arthur D. Little, Inc., Boston.

NORMAN E. HOLT, *Secretary*.

CLEVELAND SECTION.

The December meeting was held Monday, December 14th. The address of the evening was on, "Rubber and Its Manufacture," by Frank H. Van Derbeck, Manager of The Hewitt Rubber Co., Buffalo.

W. R. RIFFER, *Secretary*.

PITTSBURGH SECTION.

The one hundred and twelfth regular meeting was held Thursday, December 17th. The program was as follows: "The Freezing of Nitroglycerin and its Detonation by Shock," by Harold Hibbert, Mellon Institute; "Protein Charts," Alexander Silvermann, University of Pittsburgh; "A New Process for the Manufacture of Steel," Isador Ladoff, Westinghouse Elec. & Mfg. Co.

C. G. STORM, *Secretary*.

NASHVILLE SECTION.

The twenty-ninth meeting was held Friday, December 18th. The program was as follows: "A Few Applications of Chemistry to Fertilizer Work," by W. R. Austin.

VICTOR P. LEE, *Secretary*.

WESTERN NEW YORK SECTION.

The December meeting was held at Niagara Falls, N. Y., Thursday, the 17th. The address of the evening was on "Thermitite," by Francis A. J. Fitzgerald.

MORTIMER J. BROWN, *Secretary*.

SOUTHERN CALIFORNIA SECTION.

The regular meeting was held Thursday, November 19th, in Los Angeles. The paper of the evening was on "Cobalti-Nitrite and Its Application to the Determination of Potash," by W. B. Newkirk.

The regular monthly meeting was held Thursday, December 17th. The paper for the evening was by Dr. Stuart J. Bates, entitled "Some Chemical Effects of the Electric Discharge."

H. L. PAYNE, *Secretary*.

NEBRASKA SECTION.

The seventy-fourth regular meeting of the Nebraska Section was held Thursday, December 17th. Program: "Organic Constituents of Soils," F. W. Upson; "A New Type of Spectra," Benton Dales; "The Reading of the Fat Column in the Babcock Test," E. L. Redfern.

C. J. FRANKFORTER, *Secretary*.

GEORGIA SECTION.

The November meeting was held Saturday, November 21st. The election of officers was held, resulting as follows: *President*, Ray C. Werner, Atlanta; *Vice President*, F. I. Gibson, Savannah; *Secretary*, J. S. Brogdon, Atlanta; *Councilor*, F. N. Smalley, Savannah. The following program was given: "Some Phases of the Potash Situation," C. A. Wells; "Ground Limestone and Its Effect on Fertilizers and Soil," J. S. Brogdon; "The Injurious Action of Nitric Acid on Sulfuric Acid Chambers," E. H. Armstrong; "Sterilization of Water by Calcium Hyperchloride," Ray C. Werner.

J. S. BROGDON, *Secretary*.

UNIVERSITY OF MISSOURI SECTION.

The fifty-second meeting was held September 25th. Dr. H. Schlundt spoke upon the subject, "The Revision of Some Atomic Weights by the Radioactive Method."

The fifty-third meeting was held on October 13th. Dr. Edward Kremen of the University of Wisconsin addressed the section on the subject "Quinhydrone and their Relation to Plant Coloring Matter."

The fifty-fourth meeting was held on November 13th. Dr. C. E. Moulton spoke upon the subject, "The Preparation and Use of Neutral Ammonium Citrate Solutions."

L. D. HAIGH, *Vice-Chairman*.

The fifty-fifth meeting of the section was held on December 4th. The following officers were elected for the ensuing year: *Chairman*, Dr. L. D. Haigh; *Vice-Chairman*, Dr. Addison Gulick; *Secretary*, Miner L. Hartmann; *Treasurer*, E. E. Vanatta; *Councilor*, Prof. H. Schlundt.

MINER L. HARTMANN, *Secretary*.

DECEASED.

Wheeler, Henry L., Hartford, Conn., November, 1914.

White, Chas. N., Wilmington, Delaware, December, 1914.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN DECEMBER 15 AND JANUARY 15.

Wm., 2018 N. 22d St., Philadelphia, Pa.
Ewings, Chester E., University of Maine, Orono, Maine.
Preston P., 1609 McGavock St., Nashville, Tenn.
J. C., 521 Manhattan Ave., New York City.
H. W., 3d, Sound Beach, Conn.
C., 406 E. Healy St., Champaign, Ill.
Carl, 240 12th St., Brooklyn, N. Y.
Cedric H., 38 College House, Cambridge, Mass.
Otto F., Hammerville Paper Co., Erie, Pa.
A. W., Cr. Jones & Laughlin Steel Co., Aliquippa Wks., Wood-
a.
Jerome B., Jr., 180 Belgrave Ave., Notre Dame de Grace, Mon-
an.
Wm. O., 127 North Ave., Highland Park, Ill.
nan, Harry C., 812 6th Ave., No., Minneapolis, Minn.
h, George W., Jr., 1414 E. Columbia Ave., Philadelphia, Pa.
k, N. Henry, Roxbury Latin School, Boston, Mass.
khorn, Carl W., 5919 Olive Court, N. E., Cleveland, Ohio.
d, Lewis H., Sigma Alpha Epsilon House, Orono, Maine.
sier, Arthur H. C., 710 Langdon St., Madison, Wisc.
ek, Henry T., 508 Goepp St., Bethlehem, Pa.
ibury, Charles M., 317 East Franklin St., Richmond, Va.
uns, D. H., Maple Ave., Hyattsville, Md.
aner, C. P., 134 Barnett St., Atlanta, Ga.
ey, Richard D., 30 Church St., New York City.
wn, Anson, 391 King Ave., Columbus, Ohio.
goon, Willard T., Cleveland Wire Div., Nat'l Lamp Wks., General
ic Co., Cleveland, Ohio.
ns, James G., 486 Jarvis St., Toronto, Ont., Canada.
ler, Allen P., Bellevue, Iowa.
lenhead, A. F. G., Pickering College, Newmarket, Ont., Canada.
npbell, Arthur J., Cr. E. Pritchard, Bridgeton, N. J.
kmakjean, H. H., 37 Endicott Ave., W. Somerville, Mass.
andler, E. M. A., 1202 W. Main St., Urbana, Ill.
atfield, Charles B., 451 Orange St., New Haven, Conn.
rk, Charles L., 719 Madison Ave., Scranton, Pa.
ly, Joseph D., 440 Washington St., New York City.
llins, W. Rowland, 622 Benson St., Camden, N. J.
llwell, R. L., The Great Western Sugar Co., Longmont, Colo.
aner, Samuel D., LaFayette, Ind.
nroy, Edward H., Box 304, Iowa City, Iowa.
agg, Rollin H., 8364 Curzon Ave., Cincinnati, Ohio.
agg, William J., Cosa Colon, Huelva, Spain.
ockett, C. W., Anderson Chem. Co., Box 135, Passaic, N. J.
osby, Philip A., 2746 Dohr St., Berkeley, Calif.

- Crowell, Donald D., 28 Everett Ave., Winchester, Mass.
 Cullings, Eugene G., Hudson Heights, N. J.
 Daniels, Donald P., 1080 Beacon St., Brookline, Mass.
 Davis, Arthur R., Omega Phi House, Middletown, Conn.
 Davis, Norman Bruce, Dept. of Geology, Cornell Univ., Ithaca, N. Y.
 Dittmer, Joseph C., 286 Park Pl., Brooklyn, N. Y.
 Doan, Miss Martha, Westfield, Ind.
 Donohoe, Gerald R., 3810 Chestnut St., Philadelphia, Pa.
 Doubleday, Ralph S., 609 S. Limestone St., Lexington, Ky.
 Dunn, Fred C., 965 E. Broad St., Columbus, Ohio.
 Dunne, Wm. P., 1322 S. Travis St., Sherman, Texas.
 Eddy, Ernest A., Main and Market Sts., St. Louis, Mo.
 Elsey, H. McK., 606 Cowper St., Palo Alto, Calif.
 Epstein, Harry M., 175 Front St., New York City.
 Ernst, Herman, 174 Central Ave., E. Orange, N. J.
 Evans, Robert W., Mead Pulp & Paper Co., Chillicothe, Ohio.
 Fisher, Clayton E., Norwich University, Northfield, Vt.
 Foote, Warren M., 107 N. 19th St., Philadelphia, Pa.
 Ford, F. Edwin, 508 S. 5th Ave., Ann Arbor, Mich.
 Frey, Ralph W., Leather & Paper Lab'y., Bur. of Chem., Washington, D. C.
 Frost, John H. H., Box 890, Welland, Ont., Canada.
 Gahring, John W., 7440 Finance St., Pittsburg, Pa.
 Gartrell, Robert, 176 Park Ave., Atlanta, Ga.
 Georger, Edwin L., 609 S. Limestone St., Lexington, Ky.
 Ginslie, E. B., P. O. Box 1724, Atlanta, Ga.
 Glenn, David L., 302 So. Tacoma Ave., Tacoma, Wash.
 Glenn, T. O., 253 E. Main St., Bradford, Pa.
 Goldstein, Jacob C., 419 E. 73d St., New York City.
 Gomory, W. L., 71 Hinsdale Pl., Newark, N. J.
 Grant, Dwight A., City Asphalt Plant, Hamilton & Dallas Ave., Pittsburg, Pa.
 Griffin, Edward G., 1120 Amsterdam Ave., New York City.
 Guinther, John, Cr. Union Carbide Co. of Canada, Ltd., Welland, Ont., Can.
 Guiterman, Edward W., 337 Aycrigg Ave., Passaic, N. J.
 Gulbrandsen, S., Welsbach Co., Gloucester, N. J.
 Gutekunst, Gurney O., 1023 Oakland Ave., Ann Arbor, Mich.
 Hahn, E. L., 4858 Fountain Ave., St. Louis, Mo.
 Hahn, E. V., 2258 N. Capitol Ave., Indianapolis, Ind.
 Hahn, Fred C., 1005 So. Wright St., Urbana, Ill.
 Haigh, De Lagnel, 381 4th Ave., New York City.
 Hands, Harold E., Iowa City, Iowa.
 Harper, T. E., Jr., 706 9th Ave., Salt Lake City, Utah.
 Haskins, Harold I., 1302 Rosemont Ave., Chicago, Ill.
 Hassler, John W., 107 Oak Hall, Univ. of Maine, Orono, Maine.
 Heath, Robert H., 1131 27th Ave., Seattle, Wash.
 Hedrich, A. W., City Hall, East Chicago, Ind.
 Herman, Murray B., Marcus Hook, Del. Co., Pa.
 Herz, Alfred, 1842 Morse Ave., Chicago, Ill.
 Hickson, E. F., 74 Fern St., Bangor, Maine.
 Hines, Cleve. W., Cr. Bur. of Agriculture, Manila, P. I.

Hockett, Elmer, 83 W. Lane Ave., Columbus, Ohio.
 Houser, Clarence S., Cr. E. I. duPont Co., City Point, Va.
 Howell, John E., 402 Hathaway Ave., Houston, Texas.
 Hutchinson, Albert F., University of Maine, Orono, Maine.
 Hyde, James, 157 W. Austin Ave., Chicago, Ill.
 Jacobson, A., 2425 E. 43d St., Cleveland, Ohio.
 Jarrell, T. D., Md. Agricultural College, College Park, Md.
 Jones, D. J., 128 Union St., Scranton, Pa.
 Jones, Wm. Bartlett, 62 Fruit St., Worcester, Mass.
 Keenan, Thomas J., 117 East 24th St., New York City.
 Kempf, Norman W., 114 Bleecker St., Newark, N. J.
 Killian, John A., Fordham University, Fordham, N. Y.
 King, Walker J., 93 Dakota Ave., Columbus, Ohio.
 Kippenberg, Henry, Merck & Co., Rahway, N. J.
 Klein, Albert R., Boonton, N. J.
 Klipstein, Herbert C., 112 Newbury St., Boston, Mass.
 Kohn, Lawrence A., 45 Hamilton Terrace, New York City.
 Lewis, D. E., Y. M. C. A. Bldg., Scranton, Pa.
 Lewis, Harry F., 306 Chem. Bldg., Urbana, Ill.
 Loewith, Walter, 815 Laurel Ave., Bridgeport, Conn.
 Lupke, Paul, Jr., 771 E. State St., Trenton, N. J.
 Lyons, Roscoe C., 312 N. Denniston St., Pittsburg, Pa.
 Maag, Oscar L., 1614 Kentucky St., Lawrence, Kans.
 Macomber, M. S., Cr. Pacific Coast Condensed Milk Co., Oconomowoc,

Wisc.

Mangels, C. E., Schweitzer Hall, Columbia, Mo.
 Marvel, Carl S., 406 E. Walnut St., Bloomington, Ill.
 Maude, A. H., Cr. British Columbia Sugar Refn. Co., Ltd., Vancouver,

B. C.

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 Maverick, Phillip, Box 2115, Globe, Ariz.
 McComb, Herbert, Y. M. C. A., Gary, Ind.
 McCormack, J. H., 3336 Michigan Ave., Chicago, Ill.
 McKeague, J. Leslie, P. O. Box 246, Hudson Heights, N. J.
 Merrill, L. T., 517 Joplin St., Joplin, Mo.
 Messersmith, C. P., Fayville, Ill.
 Miller, James R., 4026 Northminster St., N. S., Pittsburg, Pa.
 Miller, W. B., Box 234, Willoughby, Ohio.
 Minis, J. C., P. O. Box 1298, New Orleans, La.
 Montgomery, John A., 1110 Paquin St., Columbia, Mo.
 Moore, Thomas E., 838 E. Bancroft St., Toledo, Ohio.
 Muench, Oscar B., 613 Turner Ave., Columbia, Mo.
 Neals, Richmond H., 4 Holland Apts., Louisa St., Oakland, Pittsburg.
 Nesbit, M. F., 1020 South Higgins Ave., Missoula, Mont.
 Northrop, John H., 1120 Amsterdam Ave., New York City.
 Novy, Robert L., Iowa City, Iowa.
 Okey, Miss Ruth E., 508 E. John St., Champaign, Ill.
 O'Shea, Thomas L., Gayville, Alexander Co., Ill.
 Osius, George, Michigan Ammonia Wks., Detroit, Mich.
 Palmer, John A., Rose Bank Apts., Pottsville, Pa.
 Patt, R. F., 1015 University Ave., Madison, Wisc.
 Patterson, C. J., 18th and Delaware Sts., Kansas City, Kans.

Paul, Alexr. G. P., 507 Linden St., Camden, N. J.
 Pettibone, C. J. V., Dept. of Physiology, Univ. of Minnesota, Minneapolis, Minn.

Porter, John J., Cr. Security Cement & Lime Co., Hagerstown, Md.
 Proescher, Frederic, Vanadium Bldg., Pittsburg, Pa.
 Puff, Raymond V., 123 Dryden Rd., Ithaca, N. Y.
 Pyman, Frank L., 6 King St., Snow Hill, London, E. C., England.
 Ramey, C. F., 2414 Dana St., Berkeley, Calif.
 Rosanoff, Martin A., Mellon Institute, Univ. of Pittsburg, Pittsburg, Pa.

Roshirt, R. J., 125 Delaware Ave., Albany, N. Y.
 Rosenbaum, R. R., 111 N. Market St., Chicago, Ill.
 Rudkin, Charles N., 256 High St., Middletown, Conn.
 Saalbach, Louis, 1436 Fifth Ave., Pittsburg, Pa.
 Sawyer, Edward E., Experiment Station, Orono, Maine.
 Saxe, Joel B., P. O. Box 1086, Montreal, Canada.
 Schultz, F. W., 2438 Grand Ave., So., Minneapolis, Minn.
 Sherman, P. L., 245 S. Los Angeles St., Los Angeles, Calif.
 Simpson, Charles A., 231 Dudley St., Boston, Mass.
 Simpson, Donald A., Princeton Rd., Douglaston, L. I., N. Y.
 Skinner, James M., Cr. Phila. Storage Battery Co., Philadelphia, Pa.
 Skirrow, F. W., Univ. of Utah, Salt Lake City, Utah.
 Smith, Leon A., 432 Bloom St., Scranton, Pa.
 Snow, L. F., 2464 H St., San Diego, Calif.
 Spray, J. H., Palisades Park, N. J.
 Stayton, S. H., 1506 S. Geddes St., Syracuse, N. Y.
 Stephens, Harry D., Lock Box 343, New Hartford, Conn.
 Stewart, Lloyd, Deane School, Santa Barbara, Calif.
 Stiff, R. M., 1008 E. 41st Place, Chicago, Ill.
 Tarver, Percy, 2095 E. 36th St., Cleveland, Ohio.
 Taylor, Hugh S., Graduate College, Princeton, N. J.
 Teague, M. C., 415 Broadway, Vincennes, Ind.
 Thelberg, John, 17 East 38th St., New York City.
 Thom, Clark C., 606 Maiden Lane, Pullman, Wash.
 Thurston, A. N., Murphysboro, Ill.
 Tredway, Miss Helen, Green Hall, Univ. of Chicago, Chicago, Ill.
 Van Arsdel, W. B., 33 Fourth St., Berlin, N. H.
 Verner, E. P., 3 Atlantic St., Charleston, S. C.
 Wadsworth, Charles, 3d, 20 Conant Hall, Cambridge, Mass.
 Wagner, C. C., Madison, So. Dak.
 Walczak, M. R., Barrett Mfg. Co., 2900 S. Sacramento Ave., Chicago, Ill.

Walter, Henry L., 1509 N. 19th St., Boise, Idaho.
 Wam, Iu-shing, 20 Caine Hall, Hongkong, China.
 Wannemacher, F. J., Cr. Stolzenbach Baking Co., Lima, Ohio.
 Webb, Edward L., 25 Prospect St., Cortland, N. Y.
 Weiland, Henry J., Chem. Lab'y, Univ. of Illinois, Urbana, Ill.
 Wells, Lansing S., 1020 So. Jiggins Ave., Missoula, Mont.
 Wheeler, Richmond, 160 Howard St., Salinas, Calif.
 Whitman, Thomas C., Jr., 74 West 5th St., Atlanta, Ga.
 Wildman, E. A., Chemistry Hall, Urbana, Ill.

Yee, G. C., Box 76, Univ. of Illinois, Urbana, Ill.
 Yeoman, Don O., 823 N. Washington St., Hutchinson, Kans.
 Zinsser, John S., Hastings-on-Hudson, N. Y.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

ST. LOUIS SECTION.

The annual meeting was held December 14th, at which the following officers for 1915 were elected: *Chairman*, Dr. L. McMaster; *Vice-Chairman*, A. C. Boylston; *Secretary*, Geo. Lang, Jr.; *Treasurer*, J. D. Robertson; *Councilor*, Dr. L. F. Nickell.

The January meeting was held Monday, the 11th. Dr. E. P. Wightman, of Washington University, addressed the Section on "Some Facts Concerning the Chemistry of Photography with Reference to the Photographic Image and Development."

GEORGE LANG, JR., *Secretary*.

SYRACUSE SECTION.

The October meeting was held October 20th. Mr. E. R. Taylor, of Penn Yan, N. Y., lectured on "Manufacture and Uses of Bisulphide of Carbon."

The November meeting was held November 24th. Mr. H. E. Howe, of Bausch & Lomb Optical Co., spoke on "Modern Spectroscopy."

The 93rd regular meeting was held December 8th. Mr. Henry A. Gardner, Assistant Director of the Institute of Industrial Research, Washington, D. C., spoke on "The Service Value of Various Painting Materials."

The 94th regular meeting was held January 5th. Dr. Arthur L. Day, Director of the Geophysical Laboratory, Washington, D. C., spoke on "The Volcano Kilauea in Action," giving illustrations.

H. B. KIPPER, *Secretary*.

LEXINGTON SECTION.

The Section held its 21st regular meeting on Wednesday, January 13th. The program: "Some Bio-Chemical Problems of the Breeder," Prof. W. S. Anderson; "Radium and Its Rays," Dr. M. H. Bedford.

LEOYD C. DANIELS, *Secretary*.

CHICAGO SECTION.

The January meeting was held January 15th. The paper of the evening was by W. G. MacNaughton, of Nekoosa-Edwards Paper Co., on "An Outline of the Manufacture of Sulfite Cellulose."

CINCINNATI SECTION.

The meeting of the Section was held January 13th. Subjects: 1. "Study of Aluminium Hydroxide as a Pigment and as a Base for Organic

Lakes"—the Hostetter Fellowship Prize essay, by Robt. F. Reed. 2. "A New Indicator of Azo Type," by Benj. E. Sibe; and 3. "Determination of the Maximum Condensation of Zinc Vapor to Liquid Zinc," by Charles L. Bloom—honorable mention essays for the same prize.

S. J. HAUBER, *Secretary*.

NASHVILLE SECTION.

The 30th meeting of the Section was held Friday evening, Jan. 15th. The program included the following paper: "Notes on the Deterioration of Hydrogen Dioxide Waters and the Effect of Acetanilide as a Retarding Catalyst," by Prof. E. A. Ruddiman.

VICTOR P. LEE, *Secretary*.

MILWAUKEE SECTION.

At the meeting of the Milwaukee Section of the A. C. S., held on December 10th, the following officers were elected: *Chairman*, Geo. N. Prentiss; *Vice-Chairman*, A. H. Gallum; *Secretary*, B. L. Solomon; *Treasurer*, F. L. Theurer; *Councilor*, Dr. A. J. Schedler.

C. R. McKEE, *Secretary*.

EASTERN NEW YORK SECTION.

The 58th meeting was held on Friday, Nov. 20th. The following paper was presented: "The Weather Bureau and Its Work," by Mr. G. T. Todd, Local Forecaster of the U. S. Weather Bureau.

The 59th meeting was held on Tuesday, Dec. 29th. The general subject of the meeting was: "Present Views of the Structure of Matter." Brief papers were presented as follows: "The Thomson and Rutherford Models of the Atom;" "The Atomic Theories of Bohr, Nicholson and Others," by Dr. Irving Langmuir; "Moseley's Work on X-Ray Spectra, Atomic Numbers, and the Nucleus Charge," by Dr. Wheeler P. Davey; "Bragg's Work on the Arrangement of Atoms in Crystals," by Dr. A. W. Hull.

At the annual election of the local section, held December 29th, the following officers for 1915 were elected: *President*, Dr. I. Langmuir; *Vice-President*, Dr. B. S. Bronson; *Sec.-Treas.*, W. E. Ruder; *Councilor*, Dr. M. A. Hunter; *Executive Committee*, W. C. Arsem, Dr. C. F. Hale, A. J. Salathe.

W. C. ARSEM, *Secretary*.

WISCONSIN SECTION.

The Wisconsin Section met on December 16, 1914. Prof. W. H. Peterson spoke on "Forms of Sulphur in Plant Materials and Their Variations with the Soil Supply." The following officers were elected for the ensuing year: *Chairman*, J. H. Mathews; *Vice-Chairman*, P. W. Carleton; *Councilor*, J. H. Walton, Jr.; *Secretary*, A. E. Koenig; *Treasurer*, W. E. Töttingham.

The January meeting was held Wednesday, January 13th. Prof. H. C. Bradley spoke on "Some Phenomena of Tissue Self-Digestion or Autolysis."

A. E. KOENIG, *Secretary*.

MINNESOTA SECTION.

The Section met Wednesday, Jan. 15th. Prof. R. W. Thatcher presented a paper on "Some Recent Biochemical Problems."

STERLING TEMPLE, *Secretary.*

LOUISIANA SECTION.

The 81st meeting was held Friday, December 18th. Program: "The Destruction of the Fly Maggot in Manure by Chemical Treatment," Dr. F. C. Cook.

The 82nd meeting was held Friday, January 15th. Program: "Manufacture of Plantation Granulated Sugar in Louisiana," Dr. Chas. E. Coater, La. State University.

J. HEATH LEWIS, *Secretary.*

CLEVELAND SECTION.

The regular meeting was held January 11th. Prof. J. R. Withrow, of the Industrial Chemistry Department of Ohio State University, gave an illustrated lecture on "Chemical Engineering of Hard Wood Distillation."

W. R. KIPPER, *Secretary.*

ROCHESTER SECTION.

The regular meeting was held Monday, December 21st. The subject for consideration was "The Practical Value of Specifications in Purchasing Coal." The viewpoint of the Chemist was presented by Wm. H. Earle, of the Gas Mfg. Dept., Rochester Railway & Light Co.; of the Consumer by W. S. Austin, Supervising Engineer for Kodak Park Works, Eastman Kodak Co.; of the Dealer by Walter H. Howard, Mgr. Yates Coal Co.

The meeting of the Section was held Monday, Jan. 4th. Dr. Arthur L. Day, Director of the Geophysical Laboratory of the Carnegie Institution, Washington, D. C., gave an illustrated lecture on "The Volcano Kilauea in Action."

H. H. TOZIER, *Secretary.*

MARYLAND SECTION.

The 4th regular meeting was held Saturday, January 16th. Program: Dr. H. Englehardt, of Sharpe & Dohme, "The Estimation of Yellow Phosphorus in Pharmaceutical Preparations." F. F. Fitzgerald, of the National Canners Association Laboratory, "The Action of Fruit Products on Tin Plate and the Preparation of Stannous Glycocolate."

FRANK M. BOYLES, *Secretary.*

KANSAS CITY SECTION.

The 105th regular meeting was held Dec. 12th. The paper of the evening was on "Color Photography and Some of Its Scientific Applications," by J. H. Mathews, of Univ. of Wisconsin. The following officers were elected for 1915: *President*, Dr. Roy Cross; *Vice-President*, Prof. W. A. Whitaker; *Councilor*, Prof. E. H. S. Bailey; *Secretary-Treasurer*, W. B. Smith; *Assistant Secretary*, Dr. C. F. Nelson.

NORTHERN INTERMOUNTAIN SECTION.

The meeting of the Section was held Saturday, December 12th. Subjects presented at that meeting were as follows: "Scientific Sympathy," Dr. Melvin A. Brannon; "The Need for Standardization of the Methods in the Wood Turpentine Industry," Mr. M. G. Donk; "The Influence of Peptones on Sugar Determinations," Geo. A. Olson.

Geo. A. Olson, *Secretary*.

NEBRASKA SECTION.

The following officers were elected at the December meeting for the coming year: *President*, Benton Dales; *Secretary-Treasurer*, H. M. Plum; *Councilor*, H. A. Senter; *Executive Committee*, F. W. Upson, George Borrowman, Jr., and Mary L. Fossler.

H. M. Plum, *Secretary*.

DECEASED.

Birley, R. K., Manchester, Eng., December, 1914.

Hall, Charles M., Niagara Falls, N. Y., December 27, 1914.

Reid, Howard E., Siegfried, Pa., December, 1914.

Stern, David, Cincinnati, O., November 9, 1914.

Rood, Ellwood D., Enid, Oklahoma, January 1, 1915.

Wright, C. W., Rock Island, Ill., January 11, 1915.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN JANUARY 15 AND FEBRUARY 15, 1915.

- Allyn, Arthur E., Jr., 1109 F. St., Lincoln, Nebr.
Backhaus, Arthur A., Dept. of Chem., Columbia University, New York City.
Bacon, John E., 196 W. Hanover St., Trenton, N. J.
Bardwell, Carlos, Box 450, Tooele, Utah.
Barnett, Chas. A., 1331 W. 112th St., Cleveland, Ohio.
Basterfield, Steward, Univ. of Sask., Saskatoon, Canada.
Bell, Hubb., The Cleveland Hardware Co., Lakeside & 45th St., Cleveland, O.
Benoliel, S. D., 4508 Locust St., Philadelphia, Pa.
Berger, W. M., 69 W. 4th Ave., Columbus, Ohio.
Bersohn, Robert, 60 E. 113th St., New York City.
Birley, John H., Chas Macintosh & Co., Ltd., Manchester, England.
Bohart, George S., 856 Middlefield Rd., Palo Alto, California.
Bosworth, Lloyd A., 315 N. Mills St., Madison, Wisc.
Brillinger, Harry E., Sigma Pi House, State College, Pa.
Brodeur, W. L., P. O. Box 181, Cooperstown, N. Y.
Callaway, Joseph, Jr., 1345 Parkwood Pl., Washington, D. C.
Campbell, Hiram D., 5751 Pierce St., Pittsburgh, Pa.
Carrell, H. G., Cr. Solvay Process Co., Syracuse, N. Y.
Chamberlain, Leslie E., Cr. General Chemical Co., Buffalo, N. Y.
Chen, Huang, 112 Pembroke St., Boston, Mass.
Christopher, F. T., Cr. Grasselli Chem. Co., P. O. Box 233, Canton, Ohio.
Clawson, John L., 240 Chestnut St., Philadelphia, Pa.
Copp, Earle M., 9 Merrill St., Barnard, N. Y.
Cowell, Chas. F., Washington, N. C.
Crane, M. B., Cr. Riverside Acid Wks., Warren, Pa.
Daby, Stanley J., 3347 Calumet Ave., Chicago, Ill.
Dale, Julian K., 3401 16th St., Washington, D. C.
Darrin, Marc, 4550 18th St., N. E., Seattle, Wash.
Davies, John R., 521 Barry Ave., Chicago, Ill.
Depew, Harlan A., 702 Church St., Ann Arbor, Mich.
Doisy, Edward A., 1003 S. Third St., Champaign, Ill.
Dunham, Henry V., Bainbridge, N. Y.
Engle, Edgar W., 311 Chem. Bldg., Univ. of Illinois, Urbana, Ill.
Erickson, Theodore, R. 7, Box 12, Murray, Utah.
Esslinger, Edwin W., Univ. of Cincinnati, Cincinnati, Ohio.
Evans, J. V. R., Badger State Tanning Co., Sheboygan, Wisc.
Faas, John C., 5220 Brooklyn Ave., Seattle, Wash.
Farnham, Roy E., Cr. The New Departure Mfg. Co., Bristol, Conn.
Farrey, Austin, 193 Sterling St., Brooklyn, N. Y.
Feldbaum, Jacob, 1501 11th St., N. W., Washington, D. C.
Field, Malcolm S., 62 Florida St., Suite 2, Dorchester, Mass.
Finch, Cecil C., Broadalbin, N. Y.
Foote, J. Wilford, 561 West 180th St., New York City.

- Franklin, C. R., 175 Sussex St., Dover, N. J.
 Freiburger, W. H., 124 W. Second St., Marion, Ind.
 Frey, Albert H., 541 Seneca St., So. Bethlehem, Pa.
 Friedemann, Wm. G., 424 Duncan St., Stillwater, Okla.
 Fulmer, Ellis G., Clark College, Toledo, Iowa.
 Gebhart, H. F., La Junta, Colo.
 Getchell, Robert W., Cedar Falls, Iowa.
 Gilson, Lewis E., Gardena, Calif.
 Gowen, Philip L., 1736 F. St., N. W., Washington, D. C.
 Grynkrut, Adolf, 1616 N. 15th St., Philadelphia, Pa.
 Hambuechen, Carl, 4 Pennsylvania Ave., Belleville, Ill.
 Harkey, Miss Tula L., 620 W. 116th St., New York City.
 Harrison, N. M., Cr. Miller Rubber Co., Akron, Ohio.
 Hassett, Paul J., Union Ribbon Factory, Bridgeport, Conn.
 Heinecke, W. W., 740 Langdon St., Madison, Wisc.
 Heist, Chas. H., 6108 Kimbark Ave., Chicago, Ill.
 Henderson, Norman H., Leechburg, Pa.
 Henry, George F., Western Springs, Ill.
 Hersey, Clarence B., Apt. 17, The Euclid, Berkeley, Calif.
 Hersh, Lewis E., Sigma Chi House, State College, Pa.
 Hodgson, Stanley F., 3801 5th Ave., Pittsburgh, Pa.
 Hoffel, A., Pl. Middenlaan 27a, Amsterdam, Holland.
 Hofmann, Heinrich O., Institute of Technology, Boston, Mass.
 Holbrook, Robert A., 194 W. 16th St., Chicago Heights, Ill.
 Holty, J. G., 522 Sunnyside Ave., Webster Groves, Mo.
 Horton, George D., Oregon Agric. College, Corvallis, Ore.
 Hoover, Donald H., Univ. of Denver, University Park, Colo.
 Howard, O. McG., Room 906, Bell Telephone Bldg., Chicago, Ill.
 Illick, E., 2156 W. 18th St., Chicago, Ill.
 Jealous, Wm. K., Rochdale, Mass.
 Johnson, Edgar B., 2155 West 101st St., Cleveland, Ohio.
 Johnson, Leslie O., P. O. Box 273, Amherst, Mass.
 Johnston, Russell R., Cr. C. R. Cook Paint Co., Kansas City, Mo.
 Kendall, S. Wilmer, 6201 Vernon Ave., Chicago, Ill.
 Kline, John H., 1307 Germantown St., Dayton, Ohio.
 Lane, Gilbert F., 176 So. Union St., Akron, Ohio.
 Lewis, Robert C., 213 Maple St., Spartanburg, So. C.
 Loomis, Albert G., 1001 Locust St., Columbia, Mo.
 Lubs, H. A., Maury Apts., 19th & G. Sts., N. W., Washington, D. C.
 Lukens, Alan R., Jr., Cr. Baltimore Roofing & Asbestos Mfg. Co.
 Asbestos, Md.
 Malmstrom, Axel, 1364 Park Blvd., Camden, N. J.
 Mann, William, 27 St. Mary Ave., London, E. C., England.
 Martin, Chas. T., 34 Forrest Ave., Chicago Heights, Ill.
 Maynard, Melvin E., 432 Lincoln Ave., Waukesha, Wisc.
 McCallum, A. L., Queen Bldg., Halifax, Nova Scotia, Canada.
 McCleery, W. L., 610 So. Main St., Santa Ana, Calif.
 Merrill, Chas. W., 121 Second St., San Francisco, Calif.
 Moore, Harry C., The Canadian Wood Distilling Co., Blaimore.
 Alta., Can.
 Morse, Guilford A., 119 Bedford St., S. E., Minneapolis, Minn.
 Nelson, Ralph A., 404 E. Healy St., Champaign, Ill.

- Nelson, R. E., 136 Grant St., West Lafayette, Ind.
 Oberhelman, G. O., 1032 High St., Grinnell, Iowa.
 Oetting, Julius H., 4944 Columbia Ave., St. Louis, Mo.
 Olsen, Miss Anna M., 610 S. Matthews Ave., Champaign, Ill.
 Pendelton, F. H., Jr., 21 High St., Malden, Mass.
 Penfield, Richard G., 198th St. & Fort Washington Ave., New York City.
 Phillips, Arthur W., 10 Prospect Hill Ave., Somerville, Mass.
 Pinkerton, Sherwood M., Jr., 624 Packard St., Ann Arbor, Mich.
 Porro, Thomas J., 4002 N. 27th St., Tacoma, Wash.
 Powers, Chas. P., 238 Semple St., Pittsburg, Pa.
 Price, Ralph A., Ford Mfg. Co., Vandalia, Ill.
 Rappold, H. E., Cr. The Grasselli Chem. Co., New Castle, Pa.
 Read, O. B., 820 W. 9th St., Cedar Falls, Iowa.
 Rhodes, Edmund O., Mellon Inst., Univ. of Pittsburg, Pittsburg, Pa.
 Richardson, Robert P., 5010 Parkside Ave., Philadelphia, Pa.
 Robertson, I. W., 240 46th St., Pittsburg, Pa.
 Rohde, Miss Alice, 104 Jackson Pl., Baltimore, Md.
 Sargent, Chas. R., 1507 Wayne Ave., Lakewood, Ohio.
 Schlosser, Walter K., Cr. Schlosser Bros., Plymouth, Ind.
 Schultz, Carl H., 308 S. Clover St., Fremont, Ohio.
 Shoemaker, C. B., 356 South Upper St., Lexington, Ky.
 Smith, Wm. Leigh, Cr. Amer. Viscose Co., Linwood P. O., Pa.
 Snyder, Forrest O., 423 W. 60th St., Chicago, Ill.
 Snyder, R. S., Soils Section, Iowa State College, Ames, Iowa.
 Stillman, Jesse W., Hartley Hall, Columbia Univ., New York City.
 Stobaeus, Wm. C., 348 Van Buren St., Newark, N. J.
 Swan, Stewart D., 1124 Amsterdam Ave., New York City.
 Tarr, Omar F., Theta Chi House, Orono, Maine.
 Taylor, Robert B., R. R. No. 5, Lexington, Ky.
 Thrun, Walter E., 509 Hitt St., Columbia, Mo.
 Townend, Robert V., Mass. Inst. of Technology, Boston, Mass.
 Tremper, Bailey, 1741 12th Ave., So. Seattle, Wash.
 Trowbridge, Milton L., 216 Ulster St., Syracuse, N. Y.
 Trozel, H. L., Cr. Masengill Bros. Co., Bristol, Tenn.
 Utzinger, Max, Toss, Ct. Zurich, Switzerland.
 Verbsky, J. F., Cr. The Grasselli Chem. Co., Lockland, Ohio.
 Vondevan, J. C., Cr. The Grasselli Chem. Co., Ltd., Hamilton, Ont.,
 Canada.
 Waddell, Robert S., 408 Starks Bldg., Louisville, Ky.
 Wahl, Arnold S., 1135 Fullerton Ave., Chicago, Ill.
 Whemhoff, Byron L., 636 No. Fife St., Tacoma, Wash.
 White, Henry L., 661 Lake St., Reno, Nevada.
 Whitehill, Warren H., Groton, Mass.
 Whitman, Earl H., 901 East River St., Pueblo, Colo.
 Wiard, Walter H., American Steel & Wire Co., Waukegan, Ill.
 Willis, A. R., Toledo Rex Spray Co., Toledo, Ohio.
 Wilsnack, George C., 7454 Stewart Ave., Chicago, Ill.
 Wolf, Edwin E., 813 East 170th St., New York City.
 Wood, Arthur E., Hamilton, N. Y.
 Wood, Harold F., 602 Monroe St., Ann Arbor, Mich.
 Woodcock, Charles M., 146 Winthrop Ave., Revere, Mass.
 Ziegelmann, G. C., 3210 Arthington St., Chicago, Ill.

MEETINGS OF THE SECTIONS.

OREGON SECTION.

At a meeting of the Section held November 28th the following officers were elected for the year: *President*, William Conger Morgan; *Vice-President*, H. V. Tartar; *Secretary*, F. A. Olmsted; *Councilor*, O. F. Stafford.

The 17th meeting was held Saturday, January 2nd. Professor O. F. Stafford of the University of Oregon gave a paper on "The Possibility of Electro-Chemical Industries in the Northwest."

At the meeting held February 6th the following papers were given: "Some Reactions of the Metal Ammonia Compounds," by R. J. Brodie; "The Application of Some-Colloids to Municipal Water Purification," by John Fulton; "The Specific Effects of Certain Fats on the Promotion of Growth," by R. A. Dutcher.

F. A. OLMSTED, *Secretary*.

MINNESOTA SECTION.

The December meeting was held December 16th. Dean G. B. Frankforter gave a talk on "Chemical Laboratories."

The following officers were elected for the year: *President*, R. W. Thatcher; *Vice-President*, F. W. Emmons; *Secretary*, Sterling N. Temple; *Treasurer*, G. Dietrichson.

W. H. HUNTER, *Secretary*.

The regular meeting was held February 19th. Program as follows: Note on "Inversion of Starch by Gaseous Hydrochloric Acid," presented by Dr. F. C. Frary. Paper on "Animal Pigments," presented by Dr. Ross A. Gortner.

STERLING TEMPLE, *Secretary*.

LOUISIANA SECTION.

Officers elected at meeting of January 15th, to serve during 1915: Mr. W. L. Howell, *President*; Mr. Geo. B. Taylor, *Vice-President*; Mr. F. W. Liepsner, *Sec.-Treas.*; Dr. Philipp Asher, *Ex-Com.*; C. E. Coates, *Councilor*.

J. HEATH LEWIS, *Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

The January meeting was held January 18th. The address of the evening was given by Professor Cyril G. Hopkins, of the College of Agriculture, University of Illinois, on "Problems in the Development of Southern Agriculture."

The February meeting was held February 16th, when the section was addressed by Dr. James H. Beal, chairman of the Board of Trustees of the U.S. Pharmacopoeial Convention on "The Pharmacopoeia and National Formulary as Legal Standards."

GEORGE D. BEAL, *Secretary*.

ROCHESTER SECTION.

The Section met January 18, 1915. Professor W. P. Mason of the Department of Chemistry, Rensselaer Polytechnic Institute, spoke on "Stored Water."

H. H. TOSIGN, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The January meeting was held January 19th. Mr. R. J. Carney gave a review of "Werner's Work on Metallic Compounds with Molecular Asymmetry."

H. H. WILLARD, *Secretary*.

PHILADELPHIA SECTION.

The regular meeting was held January 21st. The following address was given: "Radium and the Disintegration Theory of Matter" (illustrated by lantern slides), by Prof. Horace C. Richards, Department of Physics, University of Pennsylvania.

The regular meeting was held Thursday, February 18th. The following program was given: "A Study of the Reproducibility of the Cadmium Electrode," by Frederick H. Getman, Ph.D., and V. L. Gibbons. Symposium on Enzymes: "Methods of Enzyme Preparation," by Donald D. Van Slyke, A.B., Ph.D., Rockefeller Institute for Medical Research, New York City. "The Reversion of Ferment Action," by Alonzo E. Taylor, M.D., Department of Physiological Chemistry, University of Pennsylvania. "The Behavior of Enzymes at Low Temperatures," by Joseph S. Hepburn, A.M., M.S., Ph.D., formerly of Department of Biological Chemistry, Columbia University. "Ferments and Immunity," by John A. Kolmer, M.D., Dr. P. H., Laboratory of Experimental Pathology, University of Pennsylvania.

C. S. BRINTON, *Secretary-Treasurer*.

SOUTHERN CALIFORNIA SECTION.

The regular meeting was held January 21st. The paper for the evening was by Mr. Walter A. Schmidt, entitled "Experiences in the War Zone."

H. L. PAYNE, *Secretary*.

PITTSBURGH SECTION.

The 113th meeting was held January 21st. A symposium on iron and steel analysis was held as follows: 1. "Standard Methods of the U. S. Steel Corporation for the Commercial Sampling and Analysis of Plain Steels," by I. A. Nicholas, Chief Chemist, Clairton Works, U. S. Steel Corporation. 2. "The Construction of Laboratory Electric Furnaces," by C. M. Johnson, Chief Chemist, Park Works, Crucible Steel Co. of America. 3. "The Determination of Copper in Iron and Steel and the Recovery of Molybdic Acid," by W. D. Brown, Chief Chemist, Duquesne Steel Works, Carnegie Steel Co.

C. G. STORM, *Secretary*.

WASHINGTON SECTION.

At the January 21st meeting, the following papers were given: "Syntheses of Methyl and Methylamino-purines," by C. O. Johns; "Alfalfa Laccase," by H. H. Bunzel; "Concentration of Apple Juice by Freezing," by H. C. Gore.

At the February 10th meeting, F. E. Wright spoke on "The Petrographic Microscope in Analysis," and L. H. Adams spoke on "Application of the Interferometer to the Quantitative Analysis of Solutions."

E. C. McKELVEY, *Secretary*.

RHODE ISLAND SECTION.

At a meeting held January 21st, Dr. Robert F. Chambers addressed the Section on "Some Chemical Processes in Photography."

At the February 11th meeting, Dr. M. L. Crossley, of Wesleyan University, spoke on "The Future Development of the Coal-Tar Products Industry in America."

NORMAN E. HOLT, *Secretary*.

WESTERN NEW YORK SECTION.

The regular meeting was held January 22nd. Mr. Otto Mantius presented a paper upon the subject "Vacuum Evaporation."

MORTIMER J. BROWN, *Secretary*.

KANSAS CITY SECTION.

At a meeting held January 23rd the following addresses were given: "The Effect of the War on the Dye Industry," by Prof. F. B. Dains; "Gases of the Mid-continental Field," by Prof. H. C. Allen.

W. B. SMITH, *Secretary*.

CALIFORNIA SECTION.

The 83rd meeting was held January 23rd. The paper of the evening was "A Brief Review of the Work of the Selby Smelter Commission," by Ralph A. Gould, Secretary of the Commission.

BRYANT S. DRAKE, *Secretary*.

CONNECTICUT VALLEY SECTION.

The 29th meeting of the Section was held at Middletown, January 23rd, where Dr. M. L. Crossley addressed the Section on "The Development of the Dye Industry Abroad," and Dr. H. L. Ward spoke on "The Radio Elements and the Periodic Table."

On February 13th the Section inspected the plant of the Jewell Belting Company of Hartford, and Mr. F. Lee Mickle spoke on "Modern Purification of Swimming Pools."

J. C. ANDREWS, *Secretary*.

DETROIT SECTION.

At the January 29th meeting, Dr. J. E. Clark spoke to the section on "The Question of a Filtration Plant in Detroit."

At the February 18th meeting, Mr. Alexander Silverman, Director of the Department of Chemistry, University of Pittsburgh, lectured on "The Chemistry and Technology of Glass," and illustrated his talk with slides and specimens.

EDWARD J. GUTCHER, *Secretary*.

MILWAUKEE SECTION.

The Section held a meeting on January 29th. Dr. J. H. Mathews, of the University of Wisconsin, delivered an address upon "Some Advances in Processes for Color Photography," illustrated with a number of slides.

BEN L. SALOMEN, *Secretary*.

SYRACUSE SECTION.

At the 95th regular meeting of the Section, January 29th, Dr. E. S. Johnson, of the Solvay Process Company, spoke on "Aniline and its Technical Applications."

A special meeting was held Tuesday, February 2nd, when Dr. Charles L. Parsons spoke on "Radium."

The 96th regular meeting was held Friday, February 26th. Dr. J. M. Johlin, of Syracuse University, spoke on "Research Problems in the Chemistry of Forest Products."

H. B. KIPPER, *Secretary.*

NEW HAVEN SECTION.

The annual meeting was held January 29, 1915, and the following officers were elected: *President*, T. B. Johnson; *Vice-President*, R. Van Name; *Treasurer*, William Drushel; *Secretary*, G. S. Jamieson; *Councilor*, B. W. McFarland. After the election, Mr. W. H. Blauvelt, consulting engineer for the Semet Solvay Company, lectured on "The Carbonization of Coal in the By-Product Oven."

G. S. JAMIESON, *Secretary.*

ALABAMA SECTION.

The annual meeting was held January 30th. The following officers were elected: *President*, Dr. Stewart J. Lloyd; *First Vice-President*, Dr. A. H. Olive; *Second Vice-President*, Dr. J. P. Montgomery; *Secretary-Treasurer*, Dr. A. R. Bliss, Jr.; *Councilor*, Dr. B. B. Ross. The paper of the evening was "The Development of Chemical Industry in the South," by Dr. B. B. Ross.

A. R. BLISS, JR., M.D., *Secretary.*

CINCINNATI SECTION.

At the 196th regular monthly meeting held February 3rd, Dr. Moses Gomberg, Professor of Organic Chemistry, University of Michigan, delivered a lecture on "The Existence of Free Radicals."

S. J. HAUSER, *Secretary.*

CHICAGO SECTION.

The regular monthly meeting was held February 5th. The paper of the evening was "Electro-Chemical Dualism, Past and Present," by Dr. Lauder W. Jones, of the University of Cincinnati. Dr. A. A. Noyes, of Boston, was elected the recipient of the Fifth Willard Gibbs Medal, and, in pursuance of the custom in such event, will lecture before the Chicago Section at the May meeting.

D. K. FRENCH, *Secretary.*

NEW YORK SECTION.

At a joint meeting of the New York Sections of the American Chemical Society and the Society of Chemical Industry on February 5th, the subject of the evening was "The Electrochemical Production of Organic Compounds." The speakers were F. A. Lidbury, Manager, Oldbury

Electrochemical Co., "The Commercial Aspects of Organic Electrochemistry," Harold Hibbert, Mellon Institute of Industrial Research, "The Technical Production of Iodoform and other Aliphatic Compounds," (illustrated by experiments); Geo. Shannon Forbes, Professor of Electrochemistry, Harvard University, "The Electrolytic Production of Pure Coal-Tar Products," (experiments and lantern slides). C. M. JOTCH, *Secretary*.

IOWA SECTION.

The meeting of the Section was held February 6th. The program follows: "Influence of Autolysis on the Mycodextran Content of *Aspergillus Niger*," by A. W. Dox. "Observations on the Duclaux Method for Determining Volatile Aliphatic Acids," by A. R. Lamb. "Some Errors in the Gravimetric Determination of Sulfur," by P. L. Blumenthal. "Subject Selected," by C. N. Kinney.

P. A. BOND, *Secretary*.

ST. LOUIS SECTION.

At the meeting held on December 14th, Dr. L. McMaster presented a paper on "The Hydrogenation of Oils."

The regular meeting was held February 8th. Dr. P. A. Shaffer addressed the Section on "The Catabolism of Food Protein in the Animal Organism."

GEO. LANG, JR., *Secretary*.

LEXINGTON SECTION.

At the February 10th meeting, A. J. Kraemer spoke on "The Hardwood Distillation Industry," R. B. Taylor on "The Atomic Weight of Cadmium," and C. B. Shoemaker on "Acetylene Solvents."

The following officers have been elected for the year: *Chairman*, Dr. R. N. Maxon; *First Vice-President*, Dr. G. Ryland; *Second Vice-President*, Dr. W. S. Anderson; *Councilor*, Dr. A. M. Peter; and *Secretary*, Dr. L. C. Daniels.

L. C. DANIELS, *Secretary*.

MARYLAND SECTION.

The 5th regular meeting was held February 13th. Prof. Harry C. Jones, of Johns Hopkins University, addressed the Section on "The Solvate Theory of Solution."

FRANK M. BOYLES, *Secretary*.

CLEVELAND SECTION.

At the regular meeting held February 15th a talk was given on "Norton Laboratory Products."

W. R. HIPPER, *Secretary*.

DECEASED.

Birley, R. K., Manchester, England, in December, 1914.
 Crumbie, William D., East Orange, N. J., on January 16, 1915.
 Eckhardt, Dr. F., Grasselli, New Jersey, in April, 1914.
 Stiles, W. M., Long Island City, New York.

Proceedings.

COUNCIL.

President Herty appointed Professors M. C. Whitaker and Joseph W. Richards as delegates of the American Chemical Society to the meeting of the American Institute of Mining Engineers held in New York City, February 17-19, 1915.

MEMBERS ELECTED BETWEEN FEBRUARY 15TH AND MARCH 15TH, 1915.

Aisen, Maurice, 616 So. Michigan Ave., Chicago, Ill.
Angus, William, 514 Molino St., Los Angeles, Calif.
Bartlett, Edward E., 241 McKee Pl., Pittsburgh, Pa.
Bennett, W. Edgar, Reed College, Portland, Ore.
Bohn, Ralph M., 222 Spooner St., Madison, Wisc.
Brock, Clarence S., 320 Martin St., Youngstown, Ohio.
Broughton, L. B., College Park, Md.
Brunn, M. A., Cr. General Chemical Co., East St. Louis, Ill.
Burden, I. Townsend, 65 East 78th St., New York City.
Carver, Emmett K., 7 Kirkland Rd., Cambridge, Mass.
Castle, Edward A., 350 N. Clark St., Forest Park, Chicago, Ill.
Charron, A. T., Provincial Lab'y, St. Hyacinthe, P. Q., Canada.
Christie, Ralph E., 536 S. Hope St., Los Angeles, Calif.
Craig, S. J., Lake Forest, Ill.
Crebs, W. D., The Beaver Soap Co., Dayton, Ohio.
Curtis, Frederick A., Aetna Paper Co., Dayton, Ohio.
Cutler, John B., 2677 Hudson Blvd., Jersey City, N. J.
Darlington, Irwin T., 215 West 23d St., New York City.
Das Gupta, J. C., 907 N. University Ave., Ann Arbor, Mich.
Day, Robert V., 602 Lissner Bldg., Los Angeles, Calif.
De Lemon, H., Cr. Royal Baking Powder Co., 1001 Independence Blvd., Chicago, Ill.
Dicken, Clinton O., 5302 Ellis Ave., Chicago, Ill.
Dulin, R. S., 997 Cleveland Ave., Portland, Ore.
Egerey, Grete, Goucher College, Baltimore, Md.
Eichenbaum, Bertha (Miss), Corning High School, Corning, Ohio.
Estabrook, A. W., 710 Wyandotte St., Kansas City, Mo.
Faust, Henry L., 137 Clinton St., Schenectady, N. Y.
Fitch, Roy O., Y. M. C. A., Washington, D. C.
Fleming, Carl, 809 W. Grace St., Richmond, Va.
Forward, Charles C., Inland Revenue Dept. Lab'y, 50 Bedford Row, Halifax, N. S., Canada.
Gedney, Mary A. (Miss), 1952 Monroe St., Chicago, Ill.
Glass, Laurence G., 603 Queens Ave., London, Ont., Canada.
Godshalk, E. G., Cr. Bartlesville Zinc Co., Collinsville, Okla.
Greenleaf, Ralph R., 15 Nichols St., North Woburn, Mass.
Grigsby, Harry D., 1736 Hewitt Ave., Cincinnati, Ohio.
Hansen, Hugo V., 75 James St., Bloomfield, N. J.
Heath, Fay R. (Miss), Des Moines College, Des Moines, Iowa.
Hocker, Ivan S., 1717 S. St., N. W., Washington, D. C.

- Holt, Alfred, Muspratt Lab'y, University, Liverpool, England.
 Housel, Edward O., 1105 Arbor St., Champaign, Ill.
 Howell, Wm. O., 4310 Pine St., Philadelphia, Pa.
 Hunt, Louis W., Central Y. M. C. A., Cleveland, Ohio.
 Johnson, F. S., Coalton, Randolph Co., West Va.
 Kaufmann, Gustav, 432 Glennwood Ave., Ambridge, Pa.
 Kennard, Ralph B., 501 W. 110th St., New York City.
 Kern, Erwin J., 1034 First St., Milwaukee, Wisc.
 Kinzie, Charles J., Lewiston, Niagara County, N. Y.
 Knight, Harold P., Death Valley Junction, Inyo Co., Calif.
 Kolar, Gustav S., Seeley Ave. & Madison Sts., Chicago, Ill.
 MacNaughton, M. Cameron, 31 Clinton Ave., Jersey City, N. J.
 Magill, A. C., 1428 Bessie St., Cape Girardeau, Mo.
 May, R. Darwin, 1807 4th St., S. E., Minneapolis, Minn.
 McClung, John R., Sewanee, Tenn.
 McLeod, William G., Hartsville Oil Mill, Hartsville, So. Car.
 Michael, George L., 557 West 148th St., New York City.
 Middlemass, A. T. A. D., 59 Promenade, Portobello, Midlothian, Scotland.
 Miller, Edgar G., Jr., 437 W. 59th St. New York City.
 Minchivitz, Ernest U., 315 West 37th St., Los Angeles, Calif.
 Mitchell, Robert W., 53 Park Ave., Winthrop, Mass.
 Moore, Merle M., El Segundo, Calif.
 Nesbitt, Charles E., 1314 Penn Ave., Wilksburg, Pa.
 Norton, Karl B., Hastings-on-Hudson, N. Y.
 Otting, H. E., 1431 Neil Ave., Columbus, Ohio.
 Paine, Harry M., 1725 Wilson Ave., Chicago, Ill.
 Patterson, J. Edw., 618 Park Ave., Pensauken (Merchantville P. O.).
 N. J.
 Perez, R. A., 120 North Main St., Los Angeles, Calif.
 Phair, Robert A., 398 17th St., Brooklyn, N. Y.
 Plumstead, Joseph E., 20 Prospect Ave., Rumford, Maine.
 Rippel, E. G., 941 West Ave., Buffalo, N. Y.
 Rubin, Louis, 409 Decatur St., Brooklyn, N. Y.
 Scarbrough, Lewis A., 521 Lowerline St., New Orleans, La.
 Schanfelberger, William M., Stanford University, Calif.
 Seitz, Julius E., Jr., 184 Hunterdon St., Newark, N. J.
 Shoaff, Paul S., 1420 W. 47th St., Los Angeles, Calif.
 Sklarz, Leo, 556 West 181st St., New York City.
 Smith, Harold A., Reed College, Portland, Ore.
 Stapler, William W., 35 E. Springfield Ave., Champaign, Ill.
 Strack, Wallace D., 108 Hudson St., New York City.
 Strickland, Franklin N., 4 Market Sq., Providence, R. I.
 Thompson, R. C., Carnegie Steel Co., Ningo Junction, Ohio.
 Thorn, Godfrey R., Alpha Tau Omega House, State College, Pa.
 Volk, Karl E., Cr. The Amer. Agric. Chem. Co., St. Bernard, Ohio.
 Way, Pennock M., 1906 Sansom St., Philadelphia, Pa.
 Whitney, V. E., Iowa State College, Ames, Iowa.
 Whitney, W. L., Cr. U. S. Graphite Co., Saginaw, Mich.
 Wielmann, Hugo J., U. S. Food Inspection Lab'y, 518 Tabor Opera House, Denver, Colo.
 Yanovsky, Elias, Bureau of Chemistry, Washington, D. C.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons,
Box 505, Washington, D. C.]

NASHVILLE SECTION.

The thirty-first meeting was held Friday, Feb. 19th. The program included the following paper: "The Use of Methyl Sulfate in the Preparation of Some Mixed Ethers and Esters," by Victor P. Lee.

The thirty-second meeting of the Section was held March 19th. Program: "The Tennessee Food and Drug Dept. and the Laws under its Administration," by Mr. D. L. Weatherhead. *VICTOR P. LEE, Secretary.*

PHILADELPHIA SECTION.

The regular meeting was held March 18th. Program: A paper on "The Fixation of Atmospheric Nitrogen," by W. S. Landis, Chief Technologist of the American Cyanamid Company. *C. S. BRINTON, Secretary.*

ROCHESTER SECTION.

The regular meeting was held March 1st. Prof. M. C. Whitaker of Columbia University spoke on: "Relations of the Chemical Profession to Public Problems."

The regular meeting was held March 15th. The Section met in conjunction with the Rochester Electroplaters' Society, and the evening was devoted to the discussion of electroplating problems from the standpoint of the electroplater and chemist. *H. H. TOLMAN, Secretary.*

MINNESOTA SECTION.

The Section met Feb. 19th. Prof. L. J. Henderson of Harvard University lectured on "The Fitness of the Environment."

The Section met March 19th. Supt. Louis I. Birdsall of the Minneapolis Filtration Plant gave an illustrated lecture on "Water Purification." *STERLING TEMPLE, Secretary.*

NEBRASKA SECTION.

The seventy-third regular meeting of the Section was held November 7th. Program: "The Preparation and Use of Ammonium Citrate Solution in Fertilizer Analysis," by Dr. H. H. Hosford.

The February meeting of the Section was held during the week of Feb. 8th to Feb. 12th. The program consisted of a series of five lectures on "Colloid Chemistry in the Service of Biology and Medicine," by Dr. Martin H. Fischer, Professor of Physiology in the University of Cincinnati. *H. M. PLUM, Secretary.*

OREGON SECTION.

The nineteenth regular meeting was held February 27th. The following papers were presented: "The Bacterial Count of Milk," by S. A. McQueen; "The Chemical Methods for the Examination of Milk," by A. S. Wells.

F. A. OLMEYER, *Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held March 16th. Program: "The Structure of Certain Reduced Naphthoic Acids," by C. G. Derick and O. Kamm; "Oxygen Place Influence in Saturated Monobasic Paraffin Acids," by C. G. Derick and St. Elmo Brady; "The Value of Inspection Trips in the Training of a Chemist," by D. F. McFarland.

GEO. D. BEAL, *Secretary*.

WESTERN NEW YORK SECTION.

The regular meeting was held March 10th. Mr. Albert H. Hooker presented a paper upon the subject: "The Settling of Suspended Solids with Particular Reference to the Sedimentation of 'Sludge' from Bleaching Powder Solutions."

MORTIMER J. BROWN, *Secretary*.

CINCINNATI SECTION.

The one hundred and ninety-seventh regular meeting was held March 10th. The following papers were presented: "The Cotton-seed Oil Industry," by Mr. H. J. Morrison; "The Methods of Saponification of Fats," by Mr. M. B. Graff; "A Discussion of the Theory of Saponification," by Mr. Ernst Twitchell; "An Interpretation of the Properties of Free Radicals in Terms of the Electronic Conception of Positive and Negative Valences," by Dr. H. S. Fry.

STEPHAN J. HAUSER, *Secretary*.

NEW HAVEN SECTION.

The meeting was held Feb. 26th. Prof. Charles Baskerville gave a lecture on "Physical Chemistry and Anaesthesia."

GEORGE S. JAMIESON, *Secretary*.

WASHINGTON SECTION.

The two hundred and forty-sixth meeting was held March 11th. Program: W. D. Bigelow, of the National Canners Association Research Laboratory: "A Discussion of Some of the Problems and Difficulties of the Canning Industry," illustrated by moving pictures.

The two hundred and forty-seventh meeting (special) was held March 17th. Program: W. S. Landis of the American Cyanamid Company: "The Fixation of Atmospheric Nitrogen."

E. C. MCKELVY, *Secretary*.

WISCONSIN SECTION.

The March meeting was held March 11th. Professor Lawrence J.

Henderson of Harvard University spoke on "The Fitness of the Environment—The Biological Significance of the Properties of Matter."

A. E. KORNIO, *Secretary*.

CHICAGO SECTION.

At the regular meeting held March 12th, Dr. Edward Gudeman gave a paper on "Standards of Beer versus Milk."

D. K. FRENCH, *Secretary*.

DETROIT SECTION.

The regular meeting was held March 18th. Mr. Chas. T. Bragg of Berry Bros. delivered a lecture on "The Manufacture of Varnish," describing the process from the gathering of the gums to the finished product, illustrated by numerous lantern slides.

EDWARD J. GUTSCHER, *Secretary*.

CLEVELAND SECTION.

The regular meeting was held at the City Club, March 8th. Dr. O. F. Tower of Adelbert College presented a paper on "The Measurement of Vapor Pressure of Solutions." Dr. W. B. Cleveland of the Upson Nutt Co. spoke on "The Rapid Determination of Carbon in Steel."

W. R. EIFFER, *Secretary*.

MARYLAND SECTION.

The sixth regular meeting was held March 13th. Program: Dr. L. G. Rountree, Dr. E. L. Levy and Dr. W. McK. Marriott, of the Johns Hopkins Hospital: "The Reaction of the Blood, its Significance and Determination;" S. T. Powell of the Balto. County Water and Electric Co.: "The Baltimore County Water Supply."

FRANK M. BOYLES, *Secretary*.

CONNECTICUT VALLEY SECTION.

The thirty-first meeting was held March 6th. Mr. Amos Bissell, of the Essex Varnish Company, addressed the Section on "Varnishes and Japans."

J. C. ANDREWS, *Secretary*.

PUGET SOUND SECTION.

The monthly meeting was held February 27th. The address of the evening was by Mr. O. P. M. Goss of the Associated Creosoting Companies, on "Creosote and its Use in the Preservation of Timber."

H. L. TRUMBULL, *Secretary*.

SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting was held February 18th. The paper for the evening was by Dr. Julius Koebig, on "Prospects of a Chemical Industry in Southern California."

H. L. PAYNE, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The regular meeting was held February 18th. Prof. J. O. Schlotterbeck addressed the Section on "The Manufacture of Grape Juice."

H. H. WILLARD, *Secretary*.

COLUMBUS SECTION.

The regular meeting was held February 19th. Dr. Benjamin T. Brooks of the Mellon Institute, University of Pittsburgh, addressed the Section on "The Manufacture of Perfumes and Essential Oils."

WM. J. McCAUGHEY, *Secretary*.

LOUISIANA SECTION.

The eighty-third meeting was held February 19th. Program: Reports of Committee Chairmen in connection with the Spring Meeting of the American Chemical Society. A moving picture of the German Potash Mines and the "Manufacture of Potash Salts," by Dr. F. Zerban, District Representative of the German Kali Syndicate.

F. W. LIEPMER, *Secy.-Treas.*

LEXINGTON SECTION.

The Section held its twenty-third regular meeting March 11th. Program: "Decomposition Voltage of Salts in Liquid Ammonia and Some Products of Electrolysis of Ammonia Solution," by C. A. Nash; "Some Important Constituents of the Osage Orange," by J. S. McHargue.

L. C. DANIELS, *Secretary*.

NORTHEASTERN SECTION.

The Section held a meeting February 19th. Professor F. J. Moore of the Massachusetts Institute of Technology delivered an address on "The Successful Application of the Organic Point of View to the Study of Inorganic Chemistry, as Exemplified by Some of Werner's Recent Triumphs."

GRINWELL JONES, *Secretary*.

PITTSBURGH SECTION.

The one hundred and fourteenth regular meeting was held February 18th. Program: "The Behavior of Substances under Very Great Pressures," by Dr. P. W. Bridgman, Harvard University.

A special meeting was held March 12th. Mr. William A. Booth spoke on "The Chemist in Relation to Industrial Water Purification."

The one hundred and fifteenth meeting was held March 18th. Program: "A Rational Process of Fractional Distillation," by Professor M. A. Rosanoff, Mellon Institute, University of Pittsburgh.

C. G. STORM, *Secretary*.

NORTHERN INTERMOUNTAIN SECTION.

The Section held its third meeting of the year, February 13th. The program was as follows: Address by Pres. E. A. Bryan, W. S. C.; "The Influence of Irrigation on Protein Content of Wheat," by Prof. J. S. Jones and H. P. Fishburn, of U. of I.; "Nitrate Studies," by Mr. H. F. Holt, W. S. C.; "A Brief Review of Recent Investigations on Vitamines," by

Mr. H. A. Holaday, U. of I.; "The Effect of the War on the American Chemical Industry," by Dr. J. Kostalek, U. of I.

GEO. A. OLSON, *Secretary*.

CALIFORNIA SECTION.

The eighty-fourth regular meeting was held March 6th. The paper of the evening was: "Industrial Water Purification," by Dr. Otto Best.

BRYANT S. DRAKE, *Secretary*.

NEW YORK SECTION.

On page 3, March Proceedings, it should have been added that the joint meeting included the American Electrochemical Society also, and that the joint meeting was arranged through Dr. C. G. Fink, its Chairman.

The fifth regular meeting of the session of 1914-15 was held March 5th. Program: Introductory Remarks and Award of the William H. Nichols Medal to Dr Irving Langmuir, by Chairman Rogers. Dr. Langmuir then delivered an address on "Chemical Research at Low Pressures." The following officers were elected, their terms to begin at the June meeting: *Chairman*, T. B. Wagner; *Vice-Chairman*, K. G. Falk; *Sec.-Treas.*, C. M. Joyce; *Executive Committee*, Allen Rogers, B. C. Hesse, D. D. Jackson, J. M. Matthews.

C. M. JOYCE, *Secretary*.

MAINE SECTION.

The annual meeting of the Section was held in December, and the following papers were presented: "American Chemical Industry as Affected by the War," by Dr. R. H. McKee, University of Maine; "Chemical Method of Gauging Turbine Discharge," by Professor Chester Andrews, University of Maine. The following officers were elected for the coming year: *President*, W. V. Wentworth, Penobscot Chemical Fiber Company, Great Works, Maine; *Vice-President*, Mr. A. B. Andrews, Androscoggin Chemical Company, Lewiston, Maine; *Secretary and Treasurer*, Prof. E. O. Whittier, University of Maine, Orono; *Councilor*, Dr. R. H. McKee, University of Maine, Orono.

H. H. HANSON, *Secretary*.

ST. LOUIS SECTION.

The March meeting of the Section was held March 8th. The papers presented were: "The Acetolysis of Carbohydrates," by Dr. Sidney Born; "Yeasts Having Unusual Properties," by Geo. Lang, Jr.

GEO. LANG, JR., *Secretary*.

KANSAS CITY SECTION.

At the regular meeting held February 13th, the program was as follows: "Chemistry of Sewage Purification," by F. W. Bruckmiller; "The Manufacture of Clay Pipes," by Benjamin Brooks.

The March meeting was held in conjunction with the Chemical Engineers of University of Kansas, March 12. The program was as follows:

"The Technology of Clay Refractories," Paul Teetor; "Rock Salt Mining in Kansas," Sam Ainsworth; "The Chemist in Commerce," Rudolph Hirsch; "Manufacture of Portland Cement," Chris Goll; "The Milk Problem of Kansas City," Mrs. George N. Hoxie. W. B. SMITH, Secretary.

SOUTH CAROLINA SECTION.

At the regular meeting held in March, the following officers were elected to serve during the ensuing year: *President*, J. E. Mills; *Vice-President*, R. N. Brackett; *Secretary-Treasurer*, A. C. Summers; *Councilor*, Boyden Nimms. The following papers were presented: "Titration Method of Determining Neutrality of Ammonium Citrates," C. S. Lykes; "Determination of Sulfur in Pyrites by the Allen and Bishop Method," J. T. Foy; "Effect of Mixing Ground Limestone with Acid Phosphate," B. Freeman; "Urine Analysis," B. F. Robertson; "The Internal Pressure in a Liquid and a Gas," and "A Question Regarding the Kinetic Theory of Gases," J. E. Mills; "Some Chemical and Agricultural Effects of Calcium Cyanamid When Used as an Ingredient in Mixtures of Complete Fertilizers Containing Acid Phosphate," C. J. King; "Abstract of Report of Referee Nitrogen Determination, A. O. A. C.," R. N. Brackett.

A. C. SUMMERS, Secretary.

DECEASED.

Sommer, Richard, Milwaukee, Wis., February 11, 1915.

THE ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA can be furnished in different parts of Volume III, bound separately in boards, as follows: (a) Spectroscopie, \$2.00; (b) Electricite, etc., \$2.00; (c) Radioactivite, etc., \$0.50; (d) Cristallographie, etc., \$0.80; (e) Biologie, \$0.80; (f) Metallurgie, etc., \$2.00. Postage is extra. Address University of Chicago Press.

Proceedings.

GENERAL MEETING.

The Fiftieth Meeting of the American Chemical Society was held in New Orleans, Louisiana, March 31 to April 3, 1915. For the most part, the members reached New Orleans during the morning of March 31st and spent some hours in viewing the unique attractions of the city. At 4.30 P.M., 250 members and guests boarded a steamer for a trip down the Mississippi River, the usual complimentary smoker being held on the boat. The smoker was one of unusual attractions, the long cabin of the boat being festooned with Spanish moss and laurel and various Southern evergreens, making a very attractive scene. The evening was enlivened by music from two orchestras and a vaudeville troupe. The boat returned to New Orleans in time for the Council meeting held at ten o'clock P.M. at the Hotel Grunewald. On Thursday morning, April 1st, after addresses of welcome by Hon. Martin Behrman, Mayor of New Orleans, and President Robert Sharp of Tulane University, and an appropriate response from President Charles H. Herty, of the Society, the General Meeting was called to order. Professor Alfred Werner, of the University of Zurich, having been duly nominated and having received a majority vote of the Council, was elected to Honorary Membership in the Society. The meeting then listened to an address by A. D. Little on "The Industrial Resources and Opportunities of the South." Following this address, the Industrial Division held a public symposium throughout the day, presenting the following papers, all of which, with the exception of the paper by H. A. Huston, have been printed in the April, 1915, issue of the *Journal of Industrial and Engineering Chemistry*:

"Contributions of the Chemist to the Wine Industry," by Charles S. Ash, Consulting Chemist.

"Contributions of the Chemist to the Copper Industry," by J. B. F. Herreshoff, Vice-president Nichols Copper Company and Consulting Engineer General Chemical Company.

"Contributions of the Chemist to the Corn Products Industry," by E. T. Bedford, President Corn Products Refining Company.

"Contribution of the Chemist to the Asphalt Industry," by James Lewis Rake, Secretary The Barber Asphalt Paving Company.

"Contributions of the Chemist to the Cottonseed Oil Industry," by David Wesson, Manager of the Technical Department, Southern Cotton Oil Company.

"Contributions of the Chemist to the Cement Industry," by G. S. Brown, President Alpha Portland Cement Company.

"Contributions of the Chemist to the Sugar Industry," by W. D. Horne, Consulting Chemist.

"Contributions of the Chemist to the Incandescent Gas Mantle Industry," by Sidney Mason, President of the Welsbach Company.

"Contributions of the Chemist to the Textile Industry," by Franklin W. Hobbs, President Arlington Mills, and Past President American Cotton Manufacturers' Association.

"Contributions of the Chemist to the Fertilizer Industry," by H. Walker Wallace, Manager General Sales Department Virginia-Carolina Chemical Company.

"Contributions of the Chemist to the Soda Industry," by F. R. Hazard, President of the Solvay Process Company.

"Contributions of the Chemist to the Leather Industry," by William H. Teas, President Marion Extract Company.

"Contributions of the Chemist to the Flour Industry," by John A. Wessener and George L. Teller, Consulting Chemists.

"Contributions of the Chemist to the Brewing Industry," by Gaston D. Thevenot, Consulting Chemist.

"Contributions of the Chemist to the Preserved Foods Industry," by R. I. Bentley, Vice-President and General Manager California Fruit Cannery Association.

"Contributions of the Chemist to the Potable Water Industry," by Wm. P. Mason, Professor of Chemistry, Rensselaer Polytechnic Institute.

"Contributions of the Chemist to the Celluloid and Nitrocellulose Industry," by R. C. Schupphaus, Consulting Chemist.

"Contributions of the Chemist to the Glass Industry," by A. A. Houghton, Vice-President Corning Glass Works.

"Contributions of the Chemist to the Pulp and Paper Industry," by F. L. Moore, President American Paper and Pulp Association.

"The Stassfurt Potash Industry," by H. A. Huston. Illustrated with moving pictures.

A complimentary luncheon was served at the Tulane Refectory, the University being host. On Thursday evening a public address to the people of New Orleans by Bernhard C. Hesse, entitled "The Chemists' Contribution to the Industrial Development of the United States—A Record of Achievement," was given at the Hotel Grunewald, a large attendance being present. On Friday, Divisional meetings were held, before which 153 papers were presented. The details of these papers and a further description of the meetings will be found in the May issue of the *Journal of Industrial and Engineering Chemistry*. Friday evening a subscription dinner was held at the Restaurant de la Louisiane, which will long be remembered by those present for the charming company and the Creole cuisine. On Saturday one hundred of the members took a special train

to Week's Island and visited the famous salt mine of the Myles Salt Co. The train went through the bayou region of Louisiana, made famous by Longfellow's poem "Evangeline." The newly planted sugar fields and the swamps with their Spanish moss and the early tropical herbage were attractive to all. The mine, which is an unusual one, was entered by a shaft 600 feet deep, the bottom of which opened into galleries cut in solid salt many hundred feet long and 85 high by 85 feet wide, entirely unsupported by timbers. The salt, approximately 99.9% pure, is simply blasted out, carried to the surface, screened to various sizes, and placed on the market. The party returned to New Orleans in time to catch the evening trains. Many ladies were present at the meeting and under the charge of the Committee, of which Mrs. E. J. Northrup was Chairman, received many attentions from the people of New Orleans. The ladies were present at the smoker and at the banquet, took the salt mine excursion, were given a special trip through the Vieux Carré and to the Newcomb Pottery, and had a dinner of their own at one of the famous local restaurants. One hundred and seventy-five members and approximately one hundred and twenty-five guests were present, so that the meeting was a very successful one from the point of numbers, considering the distance of New Orleans from the chemical center of the country.

Meetings of the following Divisions were held. Full program will be given in May issue of the *Journal of Industrial and Engineering chemistry*.

Industrial Chemists and Chemical Engineers. H. E. Howe, in the absence of the Chairman, was in charge. The following committees were appointed:

Committee on Standard Specifications and Methods of Analysis: (Chairman not selected) A. M. Comey, J. O. Handy, Robert Job, F. G. Stantial.

Committee on Non-Ferrous Metals and Alloys, a sub-committee of the Committee on Standard Specifications: Wm. Price, Chairman, Allen Merrill, Geo. L. Heath, Gilbert Rigg, Bruno Woichiechewski.

Committee on Soap Products: Archibald Campbell, Chairman, C. P. Long, J. R. Powell, Percy H. Walker.

Committee on Glycerine, a sub-committee of the Committee on Soap Products: A. C. Langmuir, Chairman, W. H. Low, S. S. Emery, R. E. Devine, J. W. Loveland, A. M. Comey.

Committee on Naval Stores: J. E. Teeple, Chairman (other members not yet selected).

Committee on Alum: W. M. Booth, Chairman, Chas. P. Hoover, Wm. C. Carnell.

Committee on Platinum: W. F. Hillebrand, Chairman, Percy H. Walker, H. T. Allen. The full minutes of this meeting will be published

in the May issue of the *Journal of Industrial and Engineering Chemistry*.

Physical and Inorganic Chemistry. E. P. Schoch, in the absence of the Chairman, was in charge.

Fertilizer Chemistry. Chairman J. E. Breckenridge was in charge.

Agricultural and Food Chemistry. Chairman Floyd W. Robison was in charge.

Organic Chemistry. C. G. Derick, in the absence of the Chairman, was in charge.

Pharmaceutical Chemistry. Chairman F. R. Eldred was in charge.

• Biological Chemistry. Chairman C. L. Alsberg was in charge.

Water, Sewage and Sanitation. The following officers were elected: Edward Bartow, Chairman; E. B. Phelps, Vice-Chairman; H. P. Corson, Secretary; Executive Committee, the officers and C. P. Hoover and E. H. S. Bailey.

CHAS. L. PARSONS.

MINUTES OF THE COUNCIL MEETING.

The Council of the American Chemical Society met at the Grunewald Hotel, New Orleans, La., March 31, 1915, at 10 P.M., with President Herty in the Chair and with the following Councilors present: Chas. Baskerville, B. C. Hesse, E. J. Crane, Charles E. Coates, H. E. Howe, J. H. Long, Frank N. Smalley, Edward Bartow, D. K. French, W. A. Noyes, William Brady, W. D. Richardson, W. D. Bigelow, B. B. Ross, Floyd W. Robison, Chas. A. Catlin, J. S. Goldbaum, F. E. Tuttle (substitute for A. M. Peter), C. G. Derick (substitute for E. W. Washburn), L. F. Nickell, E. H. S. Bailey, Frank R. Eldred, Harry McCormick, L. H. Baekeland, George N. Prentiss (substitute for A. J. Schedler), A. D. Little, Frank R. Cameron.

It was moved that a Water, Sewage and Sanitation Division be authorized and a Division organized. A Committee consisting of W. A. Noyes, Charles E. Coates, and Edward Bartow was given power to pass for the Council on the by-laws submitted. This Committee later reported that they had examined the by-laws and found them in accord with the Constitution and approved them.

A communication from Edward C. Pickering, Chairman of a committee of the American Association for the Advancement of Science regarding expert testimony, was presented to the Council, and the Council voted the following resolution: *Resolved*, That the American Chemical Society recognizes the urgent need in the United States of reform in the methods of securing evidence of expert opinion in judicial procedure; That the American Chemical Society approves of the efforts of the American Association for the Advancement of Science in this behalf; and, That the Directors are authorized and directed to cooperate with the Committee of the American Association for the Advancement of Science in an endeavor to bring about such reforms.

A communication from the American Association for the Adoption of the Metric System, regarding the coöperation of the American Chemical Society with that association, was read, and the same was referred to the Directors of the Society and the Secretary was directed to secure more information on the subject.

Messrs. A. L. Day and C. L. Alsberg were elected Councilors-at-Large to fill out the unexpired terms of President C. H. Herty, and W. L. Dudley, deceased.

It was moved that the President appoint a committee of three to draft resolutions on the death of W. L. Dudley. A Committee consisting of Chas. Baskerville, L. H. Baekeland, and John H. Long was appointed.

A communication was received from the Chairman of the Committee on the Classification of Gas Engineering of the American Gas Institute regarding coöperation in the matter of obtaining a recognized standard of classification of engineering knowledge. It was deemed inadvisable to appoint a committee for this purpose.

A petition for the formation of a Virginia Section of the American Chemical Society, with headquarters in Richmond, Va., and a territory to include all the state of Virginia outside of Alexandria county, was received and approved. The President and Secretary were duly authorized to sign the necessary charter.

The following suggestion was presented to the Council by B. C. Hesse:

"The chemists of this country must present their claims to credit for positive industrial accomplishment in concise, clear and unmistakable form. This can be done only in the shape of a debit and credit statement; the manufacturer can then strike his balance and be governed accordingly. The main question is the credit side of the account. The symposium of nineteen papers at New Orleans is an attempt to make up such a convincing statement. In order to have the maximum of convincing power these credit statements, in the majority of cases, have been signed by executive officers of corporations. In this way the claims of the chemist are endorsed by executive officers and the carrying power of these statements increased many fold."

"Take, for example, the statement that the chemist has added between \$10.00 and \$12.00 to the value of every bale of cotton grown; or, in the wine industry, that the spoilage has been reduced from 25% to 0.46%. If, say, seventy industries could have their credit accounts appear in such concise form and endorsed by executive officers, a record would be made which would challenge any one to create a corresponding debit account."

"Seattle is making a great propaganda based upon the effect of the coming American Chemical Society meeting upon its industries. The chemist has never before been in the lime-light as he is to-day. It is, therefore,

imperative that the work begun in New Orleans be brought to a successful conclusion at Seattle. To do so, each member of the Council and of the American Chemical Society must make himself a committee of one to obtain suitable papers for industries not yet covered. All papers must be in the hands of the Editor of the *Journal of Industrial and Engineering Chemistry* not later than July 15, 1915, four months hence, so that proper publicity can be secured. If this be done, the 1915 volume of our Industrial Journal will be a reference work of great and increasing value for many years to come."

The suggestion was heartily indorsed by the Council.

A vote of thanks was passed by the Council to B. C. Hesse, Geo. P. Adamson, and M. C. Whitaker, for the very successful Industrial Symposium at the New Orleans Meeting.

A plan for the revision of the methods of keeping of chemical statistics by the United States Government was presented by B. C. Hesse, in connection with a similar proposal made to and passed by the American Institute of Chemical Engineers. It was moved that a Committee consisting of B. C. Hesse, M. C. Whitaker and the Chairman of the Division of Industrial and Engineering Chemists be appointed with power to prepare and present such a plan to the proper authorities, and this motion was duly passed.

The Council authorized President Herty to appoint delegates to the Meeting of the National Fire Protective Association to be held in New York City, May 11, 12, and 13, 1915. President Herty appointed Dr. Frederic Dannenrath as the Society's representative.

The Council was informed of the action of the Directors regarding the election of Mr. E. J. Crane as Acting Editor of *Chemical Abstracts* to fill out the unexpired term of Mr. J. J. Miller. The action of the Directors was confirmed and Mr. E. J. Crane was elected Editor of *Chemical Abstracts*.

The question of an official train to carry the members of the Society to the Seattle Meeting was presented to the Council. It was voted that the Secretary be directed to make arrangements with the officials of the Canadian Pacific road for a special train or trains to the Seattle Meeting.

A Committee consisting of J. H. Long, F. R. Eldred, Lyman F. Kebler, J. M. Francis, and B. L. Murray, appointed by President Herty to consider a proposal from the Chairman of the Commission on Proprietary Medicines of the American Pharmaceutical Association regarding co-operation with that and other associations in securing the enactment of uniform state laws taxing and regulating the traffic in opium and coca leaves and their products, reported progress and was continued.

A letter from Mr. F. R. Eldred, regarding the desirability of some method of coöperation between the various Divisions of the Society in the preparation of their programs, was presented to the Council, and it was voted

that a Committee consisting of the Chairmen of the Divisions, with the Secretary of the Society as Chairman, be instructed to consider the matter and determine whether coöperation was possible.

Reports from the following Committees were presented to the Council and are summarized below:

The Committee on Revision of Methods of Coal Sampling and Analysis reported that the second preliminary report was published by the American Society for Testing Materials last Spring. Since then further work has been done and a final report is expected this coming summer.

The Committee on Business Organization stated that their report had already been printed and distributed to the Council of the Society.

The Committee on Membership reported the acquisition of 866 new individual members and 3 corporation members during the year 1914.

The Committee on Endowment reported progress.

The Committee on Notation of Physical Chemistry recommended that the Committee be discharged, there having been no active work during the year.

The Committee on Nomenclature of Organic Chemistry reported inactivity on account of the chaotic conditions of scientific endeavor abroad.

The Committee on Inorganic Nomenclature reported that they had been in correspondence with the Committee of the International Association of Chemical Societies requesting that "columbium" be approved instead of "niobium," but that owing to foreign conditions very little progress had been made.

The Committee on Quality of Reagents reported that they found no need for their services during the past year.

The Committee on Exchanges reported that the Society has at present 171 exchanges and 14 new exchanges had been put into effect during the year. Six offers to exchange had been declined and 16 old exchanges had been discontinued.

The Perkin Medal Committee reported that they had submitted to the main Perkin Medal Committee the name of Edward Weston and Charles H. Herty for the Perkin Medal and that they had sent a letter to the President of each one of the local sections asking the coöperation of the local section in making future nominations. Their nominee, Edward Weston, received the Medal for the year 1914.

The Committee on Occupational Diseases reported progress, and that individual members of the Committee had been working in this field during the year. The Committee expected to have a well planned program and a possible symposium for the 1916 Meeting of the Society.

The Committee on Paper, through their Chairman, reported that although there had been no special work for the Committee itself to do during the year, the quality of the paper used in the Society's publications had been carefully tested from time to time and that the Editor of each Journal had been informed of the findings. The strength of the paper appears to have been below specifications and the percentage of rag not entirely up to contract requirements.

The Committee on Analysis of Potable Waters and Sewage reported that proposed modifications on extended methods of water analysis were being investigated, especially that a modified Winkler method be adopted for the determination of dissolved oxygen. Furthermore, new methods are being considered for the determination of relative stability of sewage effluents; determination of biochemical oxygen demand, and the analysis of sewage and mud deposits. It is expected that the final report will be ready for publication the latter part of the present year.

The Supervisory Committee on Standard Methods of Analysis reported as follows:

I. COMMITTEES OF THE GENERAL SOCIETY.

1. *Committee on Revision of Methods of Coal Sampling and Analysis*.—A joint committee representing the American Chemical Society and the American Society for Testing Materials.

A second preliminary report was published in the *Proc. Am. Soc. for Testing Materials* for 1914, pages 409-455. The final report is in preparation.

2. *Committee on Methods of Analysis of Potable Waters and Sewage*.—A committee of the American Chemical Society working in conjunction with one from the American Public Health Association.

The work of the above committee has been continued along the lines suggested in 1914. A report was read at the meeting of the Am. Pub. Health Assoc. at Jacksonville, Florida, December, 1914, and a report showing progress will be presented before the Section on Water, Sewage and Sanitation at the approaching New Orleans Meeting of the Chemical Society. It is expected that the final report will be ready for publication after the autumn meeting of the two societies directly interested.

II. DIVISIONAL AND SECTIONAL COMMITTEES.

A. *Division of Ind. Chem. and Chem. Eng.*—At the Cincinnati Meeting in April, 1914, it was voted by the Division of Ind. Chem. and Chem. Eng. to reorganize the committees dealing with methods of analysis and as a first step all existing committees were abolished. Certain committees have been reestablished in part with their old membership. The newly organized committees and their membership as reported to me by the Chairman of the Division, under date of February 17, 1915, are given below.

1. Committee on Standard Specifications and Methods of Analysis. A. M. Comey, Robert Job, F. M. Stantial, chairmanship not yet filled.

According to the chairman of the division this committee is supposed to control the work and to review the reports of all analysis committees within the division, but as yet this does not seem to be generally understood, for one of the other committees has submitted reports to the Supervisory Committee of the Society through the Chairman of the Division without reference to the control committee of the Division.

(a) Committee on Non-Ferrous Metals and Alloys. Wm. B. Price, Chairman, Alden Merrill, Geo. L. Heath, Gilbert Rigg, Bruno Woiciechowski.

The above committee has rendered a report on the Battery Assay of Copper, which has been approved by the Supervisory Committee on Standard Methods of Analysis and accepted for publication in the *Journal of Industrial and Engineering Chemistry*.

A report on analysis of Spelter has also been submitted and is now under consideration by the Supervisory Committee of the Society.

Preliminary work has been begun on methods for sampling and analyzing copper-bearing materials and of white metals. Other work is contemplated.

(b) Committee on Soap and Soap Products. Archibald Campbell, Chairman, C. P. Long, J. R. Powell, Percy H. Walker. The reorganized committee on Soap and Soap Products proposes to standardize methods of analysis of soaps as well as of raw materials used in the manufacture of soaps. Work on Cottonseed Products marks the beginning in this line under a special sub-committee composed as follows: W. H. Low, Chairman, F. N. Smalley, A. Campbell. No reports have been made as yet.

(c) Committee on Glycerine. A. C. Langmuir, Chairman, A. M. Comey, R. E. Divine, S. S. Emery, J. W. Loveland, W. H. Low.

This reconstituted committee, formerly a subcommittee of the original Committee on Soap and Soap Products, has during the past year co-operated with other chemists here and in Great Britain in the analysis of "Soap lye crude." The ultimate object of this work is not only to forward methods of analysis but also to fix accurately the composition of a standard sample which it is hoped will be supplied to applicants by the Bureau of Standards upon payment of a fee.

The committee is also working in coöperation with the British Glycerine Committee toward the perfection of the International Method of Analysis.

(d) Committee on Alum. Wm. M. Booth, Chairman, Chas. P. Hoover, Wm. C. Carnell.

The Committee on Alum has presented a tentative report (*J. Ind. Eng. Chem.*, 6, 435) and expects to offer a final report at the approaching New Orleans Meeting. Inasmuch as this final report will not cover

methods formulated and recommended by the committee, it does not fall within the province of the Supervisory Committee of the Society to consider it.

B. Division of Fertilizer Chemists.

1. Committee on Research and Methods of Analysis. Paul Rudnick, Chairman, F. K. Cameron, C. H. Jones, J. M. McCandless, A. J. Patten.

The above committee is a new one, formed for the purpose of taking over the work of the various committees of the Division which it replaces, namely, those on Nitrogen, Potash, Phosphoric Acid and Phosphate Rock. An extensive program of work has been mapped out and one or more preliminary reports will be presented to the Divisions at the New Orleans meeting of the Society.

C. Division of Pharmaceutical Chemists.

1. Committee on Quantitative Methods.

The above named committee has been unable to make material progress with its work during the year.

D. Section of India Rubber Chemists.

1. Committee on Analysis of Rubber and Rubber Products.

Reports and communications relating to the work of the analysis committee of the Section, but not in any way final, have appeared in the *Journal of Industrial and Engineering Chemistry*, 6, pp. 514 and 1038. Vacancies created by the resignation of Messrs. P. H. Walker and E. W. Boughton have not yet been filled.

Respectfully submitted,

(Signed) W. F. HILLEBRAND,

Chairman, Supervisory Committee on Standard Methods of Analysis.

The Finance Committee reported as follows, submitting the Treasurer's Report and the balance sheet for 1915. The Treasurer's report has already been printed in the January issue of the Journal.

"We submit herewith the Balance Sheet and Statement of the Treasurer's accounts for the year ending November 30, 1914, as certified by J. Yalden & Co., Public Accountants.

"They also state that 'the securities owed by the Society and those vested in the Morris Loeb Fund, have been verified as on hand at the Safe Deposit Vault at the Bank of Metropolis.' "

All bills presented to the Society during the year have been examined and approved by the Committee before payment.

Respectfully submitted,

(Signed) E. G. LOVE,

G. C. STONE,

A. N. HILL.

Finance Committee.

The Council then directed the Secretary to send a hearty vote of thanks to the Chairmen and members of the Committees in charge of the New Orleans Meeting for the very efficient manner in which the meeting had been handled and for the entertainment provided, and he was also directed to send the thanks of the Society to various firms and corporations that had assisted the local section in their entertainment.

The Meeting then adjourned.

CHAS. L. PARSONS, *Secretary*.

LIST OF MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15.

- Adams, Maurice, P. O. Box 51, Baton Rouge, La.
 Aliband, Alberto, Antofagasta, Chile.
 Arnell, Samuel Tomlinson, 441 Angell St., Providence, R. I.
 Atwater, C. G., 17 Battery Place, New York City.
 Baird, Thomas P., 923 E. 45th St., Chicago, Ill.
 Baringer, F. J., Eagle White Lead Co., Cincinnati, O.
 Becher, Hubert L., Agasote Millboard Co., Trenton, N. J.
 Binder, Gottfried H., 2328 Poplar St., Philadelphia, Pa.
 Breithaupt, J. E., 172 Margaret Ave., Berlin, Ontario, Canada.
 Brown, Cornelius Merrill, Williamstown, Mass.
 Cargille, R. P., 34 E. 34th St., Bayonne, N. J.
 Clark, C. E. C., J. T. Dobb & Son, Westbar, Sheffield, England.
 Crum, Bayard M., 8 Emmons Pl., New Britain, Conn.
 Davis, Philip L., 3100 Broadway, New York City.
 Dawson, Louis E., 205 E. Green St., Champaign, Ill.
 DeLaporte, A. V., 90 Gloucester St., Toronto, Canada.
 DeLong, C. R., 177 12th Ave., Columbus, O.
 Doane, Norman D., 250 W. Newton St., Boston, Mass.
 Donk, P. J., National Cannery Assn., 1739 H St., N. W., Washington, D. C.
 Eastman, Walker P., 428 N. Murry St., Madison, Wisc.
 Eavenson, Alban, 217 Atlantic Ave., Camden, N. J.
 Eovard, John M., Iowa State College, Ames, Iowa.
 Garby, Carl D., Placerville, Idaho.
 Gonder, Walter B., San José, Mindoro, P. I.
 Greeff, Robert H., R. W. Greeff & Co., Thames House, Queen St., Place, London, Eng.
 Hale, Bertrand, H., 46 Walker Bldg., Mass. Inst. of Technology, Boston, Mass.
 Heil, Henry, 210 S. 4th St., St. Louis, Mo.
 Hertz, Norman C., 3 Madison Ave., Newark, N. J.
 Hogg, Charles W., 3150 Avalon St., Pittsburgh, Pa.
 Hotchkiss, Frederic H., R. D. No. 2, Waterbury, Conn.
 Hungerford, E. H., Brookings, S. Dak.
 Jackson, Everett B., 19 Booth St., Burlington, Vt.
 Jopling, John C., 310 N. Illinois St., Indianapolis, Ind.
 Kahrs, John Fred, 3701 Tulane Ave., New Orleans, La.
 Kinney, Harrison B., Sta. A, Ames, Iowa.
 Krauss, Robert B., Henry Phipps Inst., 7th & Lombard Sts., Philadelphia, Pa.

Lewis, N. D. C., State Hospital, Crownsville, Md.
 Low, Fletcher, K. K. House, Hanover, N. H.
 Lord, Frank R., General Chemical Co., East St. Louis, Ill.
 Lowary, Ralph C., 162 Riverside Ave., Buffalo, N. Y.
 Lupton, Lewis M. G., 223 S. Broad St., Woodbury, N. J.
 Lyons, U. G., Warren, Pa.
 McCarty, Dan M., Agricultural College, Miss.
 McLavy, James R., Agricultural College, Miss.
 Meldrum, William Buell, Vassar College, Poughkeepsie, N. Y.
 Melzer, Carl, 429 W. 117th St., New York City.
 Middleton, Ellis S., 1739 H St., N. W., Washington, D. C.
 Miller, Harry G., 316 S. Henry St., Madison, Wisc.
 Moellenhoff, F. H., 5648 Morganford Road, St. Louis, Mo.
 Moss, Ernest J., 510 Int. Hypolite St., Baton Rouge, La.
 Osterhout, W. J. V., 60 Buckingham St., Cambridge, Mass.
 Perry, J. H., Delta Tau Delta, Orono, Me.
 Peterson, P. P., Moscow, Idaho.
 Plaisance, G. P., Chemical Section, Iowa State College, Ames, Iowa.
 Posey, H. G., Hurst & Webster Sts., New Orleans, La.
 Renshaw, David F., 518 W. 4th St., Tulsa, Okla.
 Renton, George F., Jr., Ewa, Hawaii.
 Richter, Ralph, 2424 S. 72d St., Philadelphia, Pa.
 Roark, G. W., Jr., College Station, Texas.
 Robinson, Edwin H., 3101 Kenwood Ave., Indianapolis, Ind.
 Rosenbaum, Eli, 1821 Diamond St., Philadelphia, Pa.
 Rudolf, T., Hotel De Soto, New Orleans, La.
 Scherer, William Franklyn, 41 Clark St., Lancaster, N. Y.
 Shaw, Morris R., Waggaman, La.
 Stedman, William, 147 N. Washington St., Hinsdale, Ill.
 Stratton, Leon D., 1130 Divinity St., West Philadelphia, Pa.
 Tully, Edward J., 1314 Spring St., Madison, Wisc.
 Weigel, Arthur G., 232 Knoblock St., Stillwater, Okla.
 Wemrich, Wm., Box 583, Honolulu, Hawaii.
 Wiggenhorn, G. F., 124 West 9th St., Los Angeles, Calif.
 Wilburn, Ballard R., 104 W. 70th St., Cincinnati, O.
 Wilson, Wm. Jas., Central Technical School, Toronto, Canada.
 Wright, Frank, 112 Kennebeck, South Kent, Washington.

MEETINGS OF THE SECTIONS

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

LOUISIANA SECTION.

The 84th meeting was held March 19th. Program: "Some Present Aspects of Pure Food Work from the Standpoint of State or Municipality," by Geo. B. Taylor, Analyst, La. State Board of Health.

F. W. LUEPNER, *Secy.-Treas.*

NASHVILLE SECTION.

The 33rd meeting of the Section was held April 16th. The program included the following paper: "The Chemistry of the Pharmacopoeia," by Mr. W. R. White.

VICTOR P. LEE, *Secretary*.

PUGET SOUND SECTION.

The March meeting was held March 27th. M. J. Falkenberg addressed the Section on "Concrete Aggregates."

H. L. TRUMBULL, *Secretary.*

UNIVERSITY OF MISSOURI SECTION.

The 57th meeting was held on February 26th in the Chemistry Building. Dr. J. W. Marden presented the results of an investigation on "The Lye Hulling of Corn for Hominy."

The 58th meeting was held April 9th. Mr. H. T. Newlon presented a paper on the "Separation of the Rare Earths," and Mr. H. L. Dahm and Mr. O. B. Muench gave "Some Notes on the Analysis of Iron and Steel."

M. L. HARTMANN, *Secretary.*

NEW HAVEN SECTION.

The regular meeting was held March 24th. Prof. Alexander Silverman, of the Chemistry Department of the University of Pittsburgh, delivered a lecture on "The Chemistry and Technology of Glass Making."

GEORGE S. JAMIESON

SYRACUSE SECTION.

A special meeting was held April 12th. Professor M. A. Rosanoff, of Pittsburgh University, spoke on "A Rational Process of Fractional Distillation."

The 98th regular meeting was held April 26th. W. R. Hulbert, M.E., spoke on "Thermit Welding."

H. B. KIPPER, *Secretary.*

DETROIT SECTION.

The regular monthly meeting was held April 15th. A. W. H. Mory, Chief Chemist of Sears, Roebuck & Co., of Chicago, gave a lecture on "The Laboratory Inspection of Merchandise."

EDWARD J. GUTSCHE, *Secretary.*

WESTERN NEW YORK SECTION.

The regular meeting was held March 26th. Prof. E. M. Chamot, of Cornell University, presented a paper upon the subject: "Some Problems in the Purification of Drinking Water from the Viewpoint of a Chemist."

The regular meeting was held April 9th. Mr. Linn Bradley presented a paper and demonstration upon the subject "Electrical Precipitation."

MORTIMER J. BROWN, *Secretary.*

CHICAGO SECTION.

The April meeting was held April 16th, at which time the Willard Gibbs Medal was awarded to Dr. Arthur A. Noyes, who gave an address on a "System of Qualitative Analysis Including Nearly all the Elements."

D. K. FRENCH, *Secretary.*

NEW YORK SECTION.

The 6th regular meeting of the session of 1914-15 was held April 9th. The program was as follows: W. A. Jacobs and Michael Heidelberger (Rockefeller Institute of Medical Research), "Contribution to the Structure of Primary and Secondary Para-Aminophenylmercuric Compounds." W. G. Lyle, L. J. Curtman and J. T. W. Marshall (College of the City of New York), "A New Test of Copper." Chas Baskerville (College of the City of New York), "Refining Vegetable Oils." M. A. Rosanoff (Mellon Institute of Industrial Research), "A Rational Process of Fractional Distillation."

C. M. JOYCE, *Secretary*.

CLEVELAND SECTION.

The regular meeting was held April 12th. Program: "The Smoke Nuisance in the Modern Industrial Community," by Raymond C. Benner, Ph.D., National Carbon Co., Fremont, O., formerly with the Mellon Institute, Pittsburgh, Pa.

A. T. BALDWIN, *Chairman and Sec. pro tem*.

PITTSBURGH SECTION.

The 116th regular meeting was held April 15th. Program: "Chemical Reactions at Low Pressures," by Irving Langmuir, of the General Electric Company Research Laboratory.

C. G. STORM, *Secretary*.

RHODE ISLAND SECTION.

The March meeting was held March 25th. The speaker for the evening was Dr. John E. Bucher, of Brown University, who addressed the Section on "The Fixation of Atmospheric Nitrogen."

NORMAN E. HOLT, *Secretary*.

CORNELL SECTION.

At the March meeting held March 26th, Professor Alexander Silverman, A.B., '05, Director of the Department of Chemistry in the University of Pittsburgh, gave a lecture, illustrated by slides and specimens, on "Chemistry and Technology of Glass."

O. R. OVERMAN, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The March meeting was held Tuesday, March 23rd. Prof. A. E. White gave a talk on "The Influence of Composition and Heat Treatment on Copper and Brass."

H. H. WILLARD, *Secretary*.

CINCINNATI SECTION.

The members of this Section accepted an invitation extended by the Dayton Engineers' Club, to attend a lecture on "Synthetic Resins," by Dr. L. H. Baekeland, April 6th.

STEPHAN J. HAUSER, *Secretary*.

NEBRASKA SECTION.

The April meeting was held April 14th. The topic for the evening was "Some Applications of Physical Chemistry in Analytical and Inorganic Chemistry," by F. W. Upson and H. M. Plum.

H. M. PLUM, *Secretary*.

ROCHESTER SECTION.

The regular meeting was held April 12th. Prof. Charles Baskerville, of The College of the City of New York, spoke on "Physical Chemistry and Anesthesia."

H. H. TOZIER, *Secretary.*

MINNESOTA SECTION.

The Section met April 16th. Professor P. M. Glasoe, of St. Olaf College, spoke on "Teaching Chemistry on the Basis of the Periodic System." Mr. L. A. Stenger, of the Twin City Rapid Transit Co., spoke on "Accuracy and Coal Analysis."

STERLING TEMPLE, *Secretary.*

MARYLAND SECTION.

The 7th regular meeting was held April 10th. Program: J. B. Rather, of the Texas Experiment Station, "Cottonseed Meal as a Human Food." Dr. C. Caspari, Jr., W. B. D. Penniman, W. W. Randall, C. O. Miller, L. H. Enslow, of the Maryland Health Department, gave papers on "Adulteration of Ground Coffee," "The Determination of Nitrites in Drinking Water and Sewage," "A General Method for Toxicological Examinations," "Apparatus for the Regulation of Temperature of Optical Instruments."

FRANK M. BOYLES, *Secretary.*

CONNECTICUT VALLEY SECTION.

The 32nd meeting was held April 3rd. Program: "Lake and Pigment Colors and Some of their Uses," A. I. Franklin. "The Harrison Law," Dr. H. C. Emerson.

J. C. ANDREWS, *Secretary.*

OREGON SECTION.

The 20th regular meeting was held March 27th. Plans for entertaining the Society for a day following the Seattle meeting next fall were discussed, and President Morgan took under advisement the appointment of a committee to make such arrangements as shall seem advisable. The following papers were presented: "Industries Using Electrolytic Processes," by H. A. Mayer. "Photographic Exposure," by H. L. Voss.

F. A. OLIMSTED, *Secretary.*

PHILADELPHIA SECTION.

The regular meeting was held April 15th. Program: A paper on "Beta Rays and the Chemical Elements," illustrated by specimens of decomposition products from radioactive substances, by Miss Fanny R. M. Hitchcock. A paper on "Metallic Tungsten," illustrated by a number of specimens of ore, etc., by Mr. Colin G. Fink, of the General Electric Company, Harrison, N. J.

C. S. BRINTON, *Secretary.*

GEORGIA SECTION.

The April meeting was held April 5th. A. D. Little, of Boston, addressed the gathering on "The Undeveloped Resources and Industries of the South."

J. S. BROGDON, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held April 23rd. Mr. Frederick W. Kressmann, of the U. S. Forest Products Laboratory at Madison, Wisconsin, addressed the Section on the subject, "The Forest Products Laboratory and Its Chemical Problems."

At a meeting held on April 24th, Mr. Kressmann spoke on the subject, "The Manufacture of Linoleum."

GEORGE D. BEAL, *Secretary*.

WISCONSIN SECTION.

The April meeting was held April 21st. The following papers were presented: "Recent Progress in the Quinone-phenolate Theory of Indicators," by Mr. E. C. White; "Some Defects in Steel Ingots," by Professor Richard S. McCaffery.

A. B. KOENIG, *Secretary*.

SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting was held April 15th. The paper for the evening was by Mr. E. O. Slater, entitled "The Sanitary Features of the Los Angeles Aqueduct."

H. L. PATTER, *Secretary*.

COLUMBUS SECTION.

A meeting was held April 16th. Mr. M. H. Williamson of the Norton Company, Worcester, Mass., addressed the Section on the "Manufacture of Alundum Refractories and Their Application in the Laboratory."

W. J. McCAUGHEY, *Secretary*.

DECEASED.

Langeloth, J., New York City, August 14, 1914.

Proceedings.

COUNCIL.

WILLIAM L. DUDLEY.

The death of Dean William Lofland Dudley, while not unexpected, was the cause of profound sorrow to many members of the American Chemical Society, of which he had been a loyal and active member since 1890.

Professor Dudley was a frequent contributor to the publications of the Society, which he served in many capacities as long as his health permitted. He also organized the Nashville Section.

Dr. Dudley was long a member of the Council, and there, as elsewhere, gained many friends, who appreciated the strong and lovable qualities which had given him great influence in education and among the youth of our country, especially in the South.

The Council of the American Chemical Society records this minute to indicate its regret and grief at the passing of one of its distinguished members—a true man in the fullest sense.

CHAS. BASKERVILLE,
LEO H. BAEKELAND,
JOHN H. LONG, *Committee.*

MEMBERS ELECTED BETWEEN APRIL 15 AND MAY 15, 1915.

Barsaloux, Lawrence F., 653 E. 105th St., Cleveland, O.
Boncquet, P. A., Spreckels Sugar Co., Spreckels, Calif.
Boyles, Page R., Box 457, Salem, Ore.
Cannon, James Lloyd, 15316 Clifton Blvd., Cleveland, O.
Cheng, G. Y., 903 Mary St., Ann Arbor, Mich.
Chewing, J. W., Box 116, Bryan, Tex.
Chichester, H. D., Springfield, Mo.
Coleman, John M., Agricultural College, Miss.
Cooke, Raymond D., 6122 Greenwood Ave., Chicago, Ill.
Dubin, Harry, 3731 Locust St., Philadelphia, Pa.
Emhardt, John C., 822 N. Front St., Reading, Pa.
Enochs, J. W., Agricultural College, Miss.
Erickson, Alf, 145 Iota Court, Madison, Wisc.
Estill, Howard W., 1727 E. Speedway, Tucson, Ariz.
Fegely, Walter H., 585 N. Main St., Meadville, Pa.
Francksen, Aug., 4803 Garden St., Bridesburg, Philadelphia, Pa.
Geidel, Carl D., 312 Clemons Ave., Madison, Wisc.
Geiger, Carl, 1223 E. Breckenridge St., Louisville, Ky.
Gibbons, Miss Vernetta L., Pembroke East, Bryn Mawr College, Bryn Mawr, Pa.
Goldman, E. L., Georgia School of Technology, Atlanta, Ga.

Habenicht, LeRoy H., Kershaw, S. C.
 Hammel, Lee A., 791 E. 158 St., Cleveland, O.
 Henton, Hugh M., Zortman, Mont.
 Homerberg, Victor O., Hopkins, Minn.
 Kellner, R. H., 6004 Hays Ave., Los Angeles, Calif.
 Lanletta, Jos. R., Jr., 1449 N. California Ave., Chicago, Ill.
 Lindfors, K. R., 612 Hoyt St., Saginaw, Mich.
 MaGuire, C. H., Chem. Lab., Lehigh University, So. Bethlehem, Pa.
 Maher, Stuart Wilder, 1210 Highland Ave., Knoxville, Tenn.
 McAllep, Will R., University Club, Los Angeles, Calif.
 McKnight, Jos. W. I., 7215 Finance St., Pittsburgh, Pa.
 Means, Karl S., 110 E. 4th St., Bloomington, Ind.
 Nakaseko, Rokuro, Doshisha Girls' School, Kyoto, Japan.
 Parrott, Albert Van Cleave, 117 So. Curtis St., Alhambra, Calif.
 Reyerson, Lloyd H., 410 Winona St., Northfield, Minn.
 Riker, Adrian, Jr., 169 Clinton Ave., Newark, N. J.
 Roberts, Emerson B., Kittanning, Pa.
 Rogers, Donald G., 16 Home St., Worcester, Mass.
 Rusch, Adolphi, Jr., 322 West 90th St., New York City.
 Rutherford, G. S., 3309 Baldwin Ave., Berwyn, Ill.
 Sanderson, T. C., Alpha Chi Sigma, State College, Pa.
 Schwoyer, John B., 316 Packer Ave., So. Bethlehem, Pa.
 Sellner, Albert, 3307 Scranton Road, Cleveland, O.
 Smith, Melville M., Apartedo 491, Barcelona, Spain.
 Snyder Electric Furnace Co., 53 West Jackson Blvd., Chicago, Ill.
 Steigman, Max, 89 Grand St. Extension, Brooklyn, N. Y.
 Stephenson, J., Gas Works, Hampton Ave., Columbia, S. C.
 Stern, Arthur L., 307 Wait Ave., Ithaca, N. Y.
 Symes, Langford Park, Belfast Freezing Works, Christchurch, New Zealand.
 Tozier, Henry H., 26 Jones Ave., Rochester, N. Y.
 Winchester, Clyde M., Edinburg, Ind.
 Yen, C. Y., 521 Post St., San Francisco, Calif.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

CONNECTICUT VALLEY SECTION.

The thirty-third meeting was held May 8th. Program: "Early References to Opium," by Dr. E. W. Morley; "The Contribution of Theoretical Chemistry to the Development of the Dye Industry," by Dr. M. L. Crossley. The following officers were elected to serve for the ensuing year: *Honorary Chairman*, E. W. Morley; *Chairman*, M. L. Crossley; *Vice-Chairman*, C. S. Williams; *Secretary*, R. J. Marsh; *Treasurer*, G. L. Clark; *Executive Committee*, H. C. Emerson, Maxwell M. Kahn, Frederic Dannerth; *Councilor*, R. B. Riggs.

J. C. ANDREWS, Secretary

GEORGIA SECTION.

On January 30th, the Savannah sub-section of the Georgia Section held a meeting in honor of President Herty, who gave an interesting address.

J. S. BROODON, *Secretary*.

CHICAGO SECTION.

The regular meeting was held May 14th. Dr. R. F. Bacon gave an address on, "Some Problems of Chemical Industry."

D. K. FRENCH, *Secretary*.

PHILADELPHIA SECTION.

The regular meeting was held May 20th. Program: "The Hydrogenation of Oils," by Carleton Ellis.

C. S. BRINTON, *Secretary*.

LEXINGTON SECTION.

The twenty-fourth regular meeting was held April 19th. Program: "Cuprous Salts of Oxygen Acids and a New Method for Preparing Cuprous Salts," by Lloyd C. Daniels.

The twenty-fifth regular meeting was held May 17th. Program: "Some Work on the Discovery and Suppression of the Illegal Sale of Narcotics in Kentucky," by J. H. Martin.

LLOYD C. DANIELS, *Secretary*.

ROCHESTER SECTION.

The regular meeting was held April 19th. Mr. Lincoln Burrows gave a talk on, "The Manufacture of Glycerine."

The regular meeting was held May 17th. Program: "Sewerage of Rochester," by John F. Skinner.

H. H. TOLZER, *Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held May 18th. Program: "The Manufacture of Sublimed White Lead and Other Lead Pigments," illustrated, by Mr. John R. MacGregor; "The Production of Lead Ore and Pig Lead and the Manufacture of Certain Lead Products," illustrated, by Mr. Fred A. Morgan.

GEO. D. BRAL, *Secretary*.

CINCINNATI SECTION.

The one hundred and ninety-eighth regular meeting was held April 21st. The following papers were presented: "General and Historical Discussion of the Soap Industry," by Howard Dock; "The Manufacture of Laundry Soaps and Soap Powders," by A. Campbell; "The Manufacture of Glycerine," by C. P. Long.

STEPHAN J. HAUSER, *Secretary*.

SYRACUSE SECTION.

A special meeting was held April 19th. Dr. F. C. Brown, Professor of Physics in the State University of Iowa, spoke on, "Selenium."

The ninety-ninth regular meeting was held May 14th. Prof. C. F. Mabery spoke on, "The Relations of the Composition of Petroleum to Its Technology."

H. B. KEEFER, *Secretary*.

LOUISIANA SECTION.

The eighty-fifth meeting was held April 16th. Program: "On the Analysis of Fertilizer Materials," by Chas. S. Williamson, Jr.; "Journal Reviews," by B. P. Caldwell and H. W. Moseley.

F. W. LIEPSCHER, *Secretary*.

CLEVELAND SECTION.

The regular meeting was held April 12th. Dr. R. C. Benner gave a talk on, "Smoke Problem in Modern Industrial Communities."

R. T. HASLAM, *Secretary, pro tem*.

The regular meeting was held May 10th. Program: "By-Products—Coke," by Caleb Davies, Jr.

A. F. O. GERMANN, *Secretary*.

ST. LOUIS SECTION.

The April meeting was held April 12th. Dr. H. M. Whelpley addressed the section on, "How the United States Pharmacopoeia is Revised."

The May meeting was held May 10th. Dr. C. M. Riley addressed the section on, "Poisons."

GEO. LANG, JR., *Secretary*.

PUGET SOUND SECTION.

The April meeting was held April 23rd. Program: An address by Mr. Darrah Corbett of Chas. C. Moore & Co., on, "The Use of Coal as a Fuel." Mr. Jas. Bagley, State Mine Inspector, presented a paper on, "Coal Production in Washington, Its Importance as an Industry, and Problems Involved in Marketing the Product."

H. L. TRUMBULL, *Secretary*.

NORTHEASTERN SECTION.

The regular meeting was held April 16th. Program: "Industrial Resources and Opportunities of the South," by A. D. Little; "Drying of Agricultural Products," by C. L. Alsberg.

GRINNELL JONES, *Secretary*.

MAINE SECTION.

The regular meeting was held May 1st. The following papers were presented: "Recent Progress in Synthetic Dyestuffs," by Mr. W. N. Watson, Instructor in Chemistry, Bates College; "A City's Milk Supply," by Mr. H. F. Ryder, Bacteriologist to the Turner Center Dairying Association; "Coal Specifications, Sampling and Analysis," by Mr. Perry Barker, Fuel Engineering Dept. of A. D. Little, Inc., Boston, Mass.; "Sodium Silicate in the Paper Mill," by Mr. J. N. Stephenson, Instructor in Chemistry, University of Maine.

E. O. WHITTIER, *Secretary*.

IOWA SECTION.

The Spring meeting was held May 1st, in connection with the meeting of the Iowa Academy of Science at Iowa City. The following program was presented: "A Comparison of the Standards of Acidimetry and Alkalimetry," by W. S. Hendrixson; "The Anston Stone from Kiveton Park, England," by Nicholas Knight; "An Important Building Stone from the Vosges Mountains," by Nicholas Knight; "Studies on Barium Sulfate," by P. L. Blumenthal and S. C. Guernsey; "A Comparison of Some Kjeldahl Methods for Nitrogen Determination," by P. L. Blumenthal and G. P. Plaisance; "A Copper Amalgam Standard Cell," by J. N. Pearce and Dieu Ung Huong; "Some Derivatives of 4-Nitro-5-Methyl-2-Sulfobenzoic Acid," by W. J. Karslake and P. A. Bond; "The Determination of Amino Nitrogen," by E. W. Rockwood and Karl Kullmann; "Viscosity of Starch Solutions and a Constant Head Viscosimeter," by H. F. Bauer.

P. A. BOND, *Secretary*.

NORTH CAROLINA SECTION.

The annual meeting of the Section was held April 19th and morning of April 20th. Dr. W. Lash Miller of the University of Toronto addressed the Section on, "Physical Chemistry." A supper was given in honor of Dr. Chas. H. Herty, President of the American Chemical Society-at large.

At the morning session the following officers were elected: *President*, Dr. J. W. Nowell, Wake Forest, N. C.; *Vice-President*, Dr. J. K. Plummer, Dept. Agr., Raleigh, N. C.; *Secretary-Treasurer*, Dr. J. T. Dobbins, West Raleigh, N. C.; *Councilor* in the American Chemical Society, Dr. A. S. Wheeler, Chapel Hill, N. C.

CHAS. E. BELL, *Secretary*.

MILWAUKEE SECTION.

The February meeting was held February 26th. Mr. F. W. Kressman gave an illustrated talk on, "Some Chemical Problems of the Forest Products Laboratory."

The March meeting was held March 26th. Prof. Harry McCormack, of Armour Institute spoke on, "The Chemist's Relation to Manufacturing Industries."

The April meeting was held April 23rd. Mr. W. W. Acheson gave an illustrated address on, "Graphite."

BEN. L. SALOMON, *Secretary*.

KANSAS CITY SECTION.

The one hundred and ninth meeting was held April 10th. Program: "The Radioactive Metals" (illustrated lecture), by Prof. H. P. Cady, University of Kansas; "Baking Powders," by Rudolph Hirsch, Ridenour-Baker Grocery Co.; "Methods Used by the Customs Service for Lead and Zinc in Ores," by C. S. Curtis, U. S. Assayer.

The one hundred and tenth meeting was held May 15th. Dr. Wm. P. Cutler of the American Manufacturers' Association of Products from Corn, spoke on, "A Practical Talk on the Products of Corn."

W. B. SMITH, *Secretary*.

OREGON SECTION.

The twenty-first regular meeting was held April 24th. The following papers were presented: "The Manufacture and Testing of Oil Gas," by W. M. Berry; "Teaching Chemistry," by Norman C. Thorne.

F. A. OLNEY, *Secretary*.

LEHIGH VALLEY SECTION.

The Spring meeting was held May 12th. Program: "Cement Industry as a Source of Fertilizer Material," by Dr. Frank K. Cameron.

GEO. C. BECK, *Secretary*.

WASHINGTON SECTION.

The two hundred and fiftieth meeting was held Thursday, May 13th. Program: "Vitamines and Beri-beri," by R. R. Williams, of the Bureau of Chemistry.

E. C. MCKELVY, *Secretary*.

WISCONSIN SECTION.

The May meeting was held May 12th. Prof. E. V. McCollum spoke on, "Recent Developments in Nutrition Study."

A. B. KOENIG, *Secretary*.

NEW HAVEN SECTION.

The regular meeting was held May 7th. Mr. Edward R. Taylor gave an illustrated lecture on, "The Manufacture and Uses of Carbon-Bisulfide, with Special Reference to the Artificial Silk Industry."

GEORGE S. JAMIESON, *Secretary*.

NASHVILLE SECTION.

The thirty-fourth meeting was held May 21st. Program: "Hydrogen Sulfide Generators," by Dr. J. I. D. Hinds; "Salvarsanized Serum in the Treatment of Locomotor Ataxia," by Wm. Litterer.

VICTOR P. LEE, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The April meeting was held April 27th. Mr. F. A. Fahrenwald presented a paper on, "Practical Substitutes for Platinum, with Especial Reference to the Use of Tungsten and Molybdenum."

H. H. WILLARD, *Secretary*.

UNIVERSITY OF MISSOURI SECTION.

The regular meeting was held Friday, May 7th. Prof. H. P. Cady, of the University of Kansas, gave a special lecture on, "The Occurrence of Helium in Natural Gas."

M. L. HARTMANN, *Secretary*.

ALABAMA SECTION.

The regular meeting was held May 8th. Prof. Jack P. Montgomery presented a paper entitled: "The Effect of Lock 17 on the Water Supply of Tuscaloosa."

A. R. BLISS, JR., *Secretary*.

NORTHERN-INTERMOUNTAIN SECTION.

The Section held its last meeting for this fiscal year, April 24th. The following program was rendered: "The Effect of the War on the American Chemical Industry," by Dr. J. Kostalek, U. of I.; "The Wet Assay of Copper," by Prof. Elton Fulmer, W. S. C.

The officers for the ensuing year were elected as follows: *Chairman*, C. L. von Ende; *Secretary-Treasurer*, Geo. A. Olson; *Vice Chairman*, C. M. Brewster; *Councilor*, J. S. Jones.

GEO. A. OLSON, *Secretary*.

SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting was held May 20th. The paper for the evening was by Dr. W. P. Kelley, entitled, "Nitrogen from the Standpoint of Plant Nutrition."

H. L. PAYNE, *Secretary*.

PITTSBURGH SECTION.

The one hundred and seventeenth regular meeting was held May 20th. Program: "The Use of Barium Compounds in Glass," by Professor Alexander Silverman, Director Department of Chemistry, University of Pittsburgh; "The Determination of Vapor Pressures of Gases at Low Temperatures," by G. A. Burrell, U. S. Bureau of Mines.

C. G. STORM, *Secretary*.

VAN'T HOFF FUND.

According to the regulations of the Van't Hoff Fund, founded June 28, 1913, interested persons are sent the following information:

The foundation, with headquarters at Amsterdam, is under the supervision of the Royal Academy of Sciences, and grants each year, before the 1st of March, from the income of the fund, certain sums to investigators in the field of pure and applied chemistry who have applied for same before November 1st of the previous year. At the present time the Committee in charge of the fund consists of A. F. Holleman (*President*), S. Hoogewerff, A. Smits, F. M. Jaeger (*Secretary*), to whom applications should be addressed.

The Committee has the privilege of enlarging its membership by the appointment of others for one-year terms. The names of grantees will be published. Any individuals who have received a grant are expected to send to the Committee copies of papers relating to the results of their work, but they are otherwise at liberty to choose the manner and place of publica-

tion, with the simple requirement that they mention the fact that the research was made from an endowment received under the Van't Hoff Fund.

The amount available for 1916 will be approximately \$520. In 1915, a grant of six hundred francs was made to Dr. D. E. Tsakalotos, of Athens, Greece, for "investigations on the viscosity and magnetism of binary mixtures, which can deposit endothermic compounds."

Applications should be sent, registered by post, to: Het Bestuur der Koninklyke Akademie van Wetenschappen; bestemd Voor de Commissie van het "Van't Hoff fonds," Trippenhuys, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, and of the reasons on which the candidates ground their claim.

In the name of the Committee of the "*Van't Hoff Fund*."

A. F. HOLLEMAN, *President*.

F. M. JAEGER, *Secretary*.

Amsterdam, the month of April, 1915.

Proceedings.

COUNCIL.

The following committees have been appointed by President Herty for the coming year. According to the Constitution, their duties terminate with the Spring Meeting of 1916:

Annual Report on Atomic Weights: G. P. Baxter.

Business Methods: Charles Baskerville, *Chairman*, A. D. Little, A. Lowenstein, C. E. Caspari, F. K. Cameron.

Denatured Alcohol: C. A. Crampton, *Chairman*, G. P. Adamson, A. M. Breckler.

Endowment: George D. Rosengarten, *Chairman*, Isaac King Phelps, G. F. Kunz.

Exchanges: E. J. Crane, *Chairman*, W. A. Noyes, M. C. Whitaker.

Finance Committee: E. G. Love, *Chairman*, G. C. Stone, A. E. Hill.

Inventions by Government Employees: L. H. Baekeland, Wm. M. Grosvenor.

Membership: Frank K. Cameron, *Chairman*, W. D. Bigelow, Charles L. Parsons.

Methods of Analysis for Potable Waters and Sewage: Edward Bartow, *Chairman*, W. P. Mason, H. E. Jordan, E. H. S. Bailey, W. W. Skinner.

Occupational Diseases: Charles Baskerville, *Chairman*, G. P. Adamson, H. K. Benson, C. E. Coates, W. L. Evans, F. W. Frerichs, Edw. Gudeman, M. I. Hersey, E. B. Phelps, S. R. Scholes, F. N. Smalley, H. W. Gillette.

Paper: F. P. Veitch, *Chairman*, W. A. Noyes, A. D. Little, M. C. Whitaker, E. J. Crane, Vasco Nunez.

Patent and Related Legislation: L. H. Baekeland, *Chairman*, E. A. Hill, A. D. Little, W. R. Whitney, C. P. Townsend, Carleton Ellis.

Perkin Medal: M. C. Whitaker, *Chairman*, G. E. Barton, C. E. Munroe, T. B. Wagner, A. M. Comey, R. H. McKee, I. M. Bregowsky, J. R. Withrow.

Revision of Methods of Coal Sampling and Analysis: W. A. Noyes, *Chairman*, A. H. White, Perry Barker, W. F. Hillebrand, A. C. Fieldner.

Supervisory Committee on Standard Methods of Analysis: W. F. Hillebrand, *Chairman*, Clifford Richardson, G. C. Stone, H. P. Talbot.

Uniform State Laws for Regulating Traffic in Opium and Coca Leaves, Etc.: J. H. Long, *Chairman*, F. R. Eldred, L. F. Kebler, J. M. Francis, B. L. Murray.

MEMBERS ELECTED BETWEEN MAY 15 AND JUNE 15, 1915.

Baker, Elbert C., 2 Central Ave., Ithaca, N. Y.
 Barnard, John F., Carthage, Mo.
 Bhudkamkar, P. P., 554 West 114th St., New York City.
 Booth, Harold S., 7107 Clinton Ave., N. W., Cleveland, O.
 Caldwell, E. K., 6728 Dorchester Ave., Chicago, Ill.
 Charron, Roy Chester, 426 Newburg St., Boston, Mass.
 Davies, John Burton, 1536 Highland Ave., Lakewood, O.
 Derr, E. W., Massena, N. Y.
 Driscoll, J. E., 224 E. 34th St., Savannah, Ga.
 Ducray, Raymond G., Box 51, Baton Rouge, La.
 Eyler, John D., 3416 Mondawmin Ave., Walbrook, Baltimore, Md.
 Flaks, Julius, 4634 N. Robey St., Chicago, Ill.
 Gibbs, Joseph H., Jordan, N. Y.
 Gillson, Joseph L., 706 Forest Ave., Wilmette, Ill.
 Hixson, Arthur W., 1024 E. College St., Iowa City, Ia.
 Kemp, Emma L., 366 Webster Ave., Jersey City, N. J.
 Kuttner, Theodore, 15 Central Park West, New York City.
 Lippincott, Wilmot C., Cherry River Paper Co., Richwood, W. Va.
 Lutes, Neil T., 252 No. Gal. Ave., Freeport, Ill.
 Marceau, Eugene T., 5468 Blackstone Ave., Chicago, Ill.
 McConnell, J. R., 471 Manhattan Ave., New York City.
 Morgan, Henry S., 673 Rutherford Ave., Trenton, N. J.
 Morse, Henry E., 448 Columbia Ave., Palmerton, Pa.
 Mosconyi, Emilio, Box 158, San Salvador, San Salvador, C. A.
 O'Brien, John F., 215 5th Ave., Mechanicsville, N. Y.
 Rew, Geo. C., 4100 Fillmore St., Chicago, Ill.
 Slocum, F. L., 401 S. Linden Ave., Pittsburgh, Pa.
 Smith, Mabel, 1110 East 64th St., Chicago, Ill.
 Stillwagon, S. C., 2637 Grand Ave., Chicago, Ill.
 Thorburn, Robert R., 1801 Reid St., Los Angeles, Calif.
 Urquhart, George G., 4217 Pine St., Philadelphia, Pa.
 Weer, George L., Newport, Del.
 Weidig, J. Kleinhans, 206 Clifton Ave., Newark, N. J.
 Weinik, Samuel, 1770 Madison Ave., New York City.
 Woliung, Wm., Jarechi Chemical Co., Sandusky, O.
 Yonge, Wm. K., 135 River Ave., San Antonio, Texas.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons,
 Box 505, Washington, D. C.]

UNIVERSITY OF MISSOURI SECTION.

The sixtieth regular meeting was held May 21. Mr. Benjamin E. Sive
 spoke on "A New Indicator of the Azo Type." M. L. HARTMANN, Secretary.

PHILADELPHIA SECTION.

The regular meeting (the last until October) was held June 19.

Program: "Photography in Natural Colors," by Dr. Henry Leffmann,
 Philadelphia. C. S. BRINTON, Secretary.

MILWAUKEE SECTION.

The meeting held by the Milwaukee Section on May 19 was devoted to showing moving pictures of the following industries:

"Making Pulp and Paper," by the Minnesota and Ontario Power Company.

"Making Pure Food Products," by the H. J. Heinz Company.

"The Fixation of Atmospheric Nitrogen," by the American Cyanamid Company.

BEN L. SALOMON, *Secretary*.

NEW YORK SECTION.

The seventh regular meeting of the session of 1914-15 was held in conjunction with the New York Sections of the Soc. of Chem. Ind. and the Am. Electrochem. Soc. under the auspices of the Soc. of Chem. Ind. on May 21. The program was as follows:

"The Cracking of Petroleum," Benjamin T. Brooks.

"A Convenient Form of Receiver for Fractional Distillation under Diminished Pressure," Marston T. Bogert.

"The Synthesis of the Cymene Carboxylic Acids," J. R. Tuttle and Marston T. Bogert.

The eighth regular meeting of the session of 1914-15 was held June 11. The program was as follows:

"Studies on Amylases VIII-XII," H. C. Sherman, M. D. Schlesinger, A. W. Thomas, A. P. Tanberg and P. W. Punnett.

"Nephelometry (Photometric Analysis) I. History of Method and Demonstration of Instruments," Philip A. Kober.

"On the Rate of Evaporation of Ether from Oils and Its Application in Oil-Ether Anesthesia," Chas. Baskerville.

C. M. JOYCE, *Secretary*.

PITTSBURGH SECTION.

The one hundred and eighteenth regular meeting was held June 17.

Program: "Portland Cement: Its Composition, Properties, and Its Relation to Other Hydraulic Cements," by P. H. Bates, U. S. Bureau of Standards.

C. G. STORM, *Secretary*.

CORNELL SECTION.

The Section met May 31.

Program: "The Fractional Electrolysis of Solutions of the Rare Earths," by P. A. van der Meulen.

"The Determination of Minute Amounts of Arsenic," by F. R. Georgia.

"Binary Systems: Ammonia, Sodium Chloride; Ammonia, Sodium Bromide; Ammonia, Sodium Iodide," by I. E. Lee.

At the meeting of May 31, the following officers were elected to serve for the ensuing year: T. R. Briggs, *President*; S. A. Mahood, *Vice-President*; J. A. Bridgman, *Sec.-Treasurer*; *Executive Committee*, Officers and T. W. B. Welsh, F. E. Rice, P. A. van der Meulen.

O. R. OVERMAN, *Secretary*.

SOUTHERN CALIFORNIA SECTION.

The June meeting was held June 15 at Eighth and Broadway. It was a joint meeting with the societies of Civil Engineers, Electrical Engineers, Mechanical Engineers, Mining Engineers, Architects, and Engineers and Architects, and American Chemical Society of Los Angeles.

The meeting was addressed by Wm. Mulholland and by Dr. James A. B. Scherer, president of Throop College of Technology, on the subject, "Service of the Technical Man to the Community."

H. L. PAYNE, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The last meeting of the Section was held June 1. Papers were given by Mr. L. H. Greathouse on "The Use of Periodates in Quantitative Analysis," and by Mr. H. T. Hood on "The Carbonization of Steel by Means of Gas."

H. H. WILLARD, *Secretary*.

DETROIT SECTION.

At the Annual Meeting, held May 20, the following officers were elected to serve during the ensuing year: Charles T. Bragg, *President*; Howard T. Graber, *Vice-President*; Edward J. Gutsche, *Secretary*; James H. Bogart, *Treasurer*.

EDW. J. GUTSCHE, *Secretary*.

NASHVILLE SECTION.

At the May meeting the following officers were elected to serve for the ensuing year: Prof. J. I. D. Hinds, *Chairman*; Prof. E. A. Ruddiman, *Vice-Chairman*; Victor P. Lee, *Secretary-Treasurer*; *Councilor*, Prof. W. H. Hollinshead.

VICTOR P. LEE, *Secretary*.

SOUTH CAROLINA SECTION.

The third meeting of the Section was held May 28.

Program: R. N. Brackett (read by Mr. Wm. G. McLeod), "Determination of Lint in Cottonseed Meal." E. P. Venner (read by Mr. J. W. Rhea), "The Position of the Chemist in the Industries." R. M. Simpson, "Determination of Crude Fiber." Boyden Nims, "Enzymes." C. W. Rice, "Determination of Sulfur in Pyrites Ore." A. C. Doyle, "Adulteration of Drugs." J. E. Mills, "The Specific Heat of the Elements." Dr. F. A. Coward, "Disinfectants." J. E. Mills, "On Some Pressure—Volume—Temperature Relations."

A. C. SUMMERS, *Secretary*.

WESTERN NEW YORK SECTION.

On May 26 the Section attended a meeting of the Buffalo Academy of Medicine, Section of Pathology, at which was presented "A New Conception of the Physical Basis of Life," with experimental demonstration, by Dr. G. H. A. Clowes.

The following officers were elected to serve for the ensuing year: Lewis E. Saunders, *President*; J. A. Miller, *1st Vice-President*; J. G. Melendy, *2nd Vice-President*; Ray H. White, *Secretary*; R. C. Snowdon, *Treasurer*; Walter Wallace and W. H. Watkins, *Councilors*.

M. J. BROWN, *Secretary*.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN JUNE 15 AND JULY 15, 1915.

Bache, William A., 1912 No. 21st St., Philadelphia, Pa.
Bright, H. A., 1437 Belmont St., Washington, D. C.
Briscoe, Henry V. A., 33 Bargerey Rd., Catford, S. E., England.
Brundage, Edward F., Thomsen Chemical Co., Baltimore, Md.
Chiu, Yan Tsz, Canton Christian College, Canton, China.
D'Eustachio, Gabriele G., 175 Water St., Perth Amboy, N. J.
Dunning, W. G., Hudson Heights, N. J.
Ferguson, George E., 315 West 137th St., New York City.
Fourness, C. A., Cr. Kimberly-Clark Co., Kimberly, Wisc.
Georgia, F. R., Morse Hall, Ithaca, N. Y.
Hartzell, Arthur R., 130 N. 9th St., Allentown, Pa.
Hoffman, A. F., 622 Kirtland St., Pittsburg, Pa.
Holmes, James E., 1308 Linden Ave., Baltimore, Md.
Kelly, James A., 406 Nutts Ave., Phoenixville, Pa.
Kraybill, Henry R., Box 413, State College, Pa.
Lennox, Frank J., 48 Front St., Woonsocket, R. I.
MacMichael, R. F., Auburn, Wash.
Marshall, Albert E., 50 E. 41st St., New York City.
Mayer, Otto, Jr., Box 133, Sheffield, Pa.
Morgan, Henry H., Jr., Parlin, N. J.
Pfeil, Ralph T., 4261 Viola St., Philadelphia, Pa.
Plate, Richard P., 115 Morris St., Jersey City, N. J.
Roscoe, Harry R., 305 Norton St., Kansas City, Mo.
Ryan, Roger W., Auburn, Wash.
Spangler, Samuel F., 1230 N. 41st St., Philadelphia, Pa.
Stockinger, Otto E., Winyah Sanatorium, Asheville, N. C.
Walsh, James F., 81 Buena Vista Ave., Yonkers, N. Y.
Walter, Robinson F., 424 Pawnee St., So. Bethlehem, Pa.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

OREGON SECTION.

The twenty-second regular meeting was held May 29. Mr. Walter P. Shuck presented a paper on "Electrolytic Process for the Manufacture of Oxygen and Hydrogen."

F. A. OLMSTED, *Secretary*.

CHICAGO SECTION.

At the meeting held May 14 the following officers were elected to serve the Section for the ensuing year: *Chairman*, W. D. Harkins; *1st Vice-Chairman*, L. I. Shaw; *2nd Vice-Chairman*, F. L. Dunlap; *Secretary*, D. K. French; *Treasurer*, O. Eisenschiml.

The June meeting was held June 11. Program: "Some Notes on Permutit," D. K. French; "Some of the Ductless Glands during Intra-Uterine Life," Frederick Fenger; "Crude Fiber in Prepared Mustard," C. L. Munroe; "Oil Fires in the Texas and Oklahoma Districts," G. B. James.

D. K. FRENCH, *Secretary*.

ALABAMA SECTION.

The regular meeting was held on the evening of May 8th. The paper of the evening: "The Effects of Lake Bankhead on the Water Supply of Tuscaloosa, Alabama," by Dr. Jack P. Montgomery.

A. R. BLISS, JR., *Secretary*.

EASTERN NEW YORK SECTION.

A meeting of the Section was held Friday evening, May 28th. The address was given by Dr. J. M. Nelson, Professor of Organic Chemistry, Columbia University, who spoke on "The Election Conception of Valence."

W. E. REEDER, *Secretary*.

ST. LOUIS SECTION.

The June meeting was held Monday evening, the 14th, at the American Hotel. Dr. Caspari brought up a question of professional ethics which led to a discussion on ethics which took up the major portion of the evening. Attendance, 23. At the dinner, 16.

GEO. LANG, JR., *Secretary*.

PITTSBURGH SECTION.

The one hundred and eighteenth regular meeting was held June 17.

W. C. Cope was elected Secretary, vice C. G. Storm, resigned, and Charles E. Nesbitt was elected Treasurer, vice C. A. Lambert, resigned, both retiring officers resigning on account of leaving the city.

The paper of the evening, "Portland Cement: Its Composition, Properties, and Its Relation to Other Hydraulic Cements," was given by P. H. Bates, United States Bureau of Standards, illustrated by lantern slides.

A two-reel motion picture, prepared by the United States Bureau of Mines, was projected, showing method of manufacture of Portland cement at the Dickinson, Ill., plant of the Marquette Cement Company.

W. C. COPE, *Secretary*.

DECEASED.

Albert Plaut, 120 William St., N. Y. City, June, 1915.

F. W. Spanutius, Hastings-on-Hudson, N. Y., June 20, 1915.

Proceedings.

COUNCIL.

President Herty appointed Drs. Edmund O'Neil, E. C. Franklin, and H. K. Benson delegates of American Chemical Society to San Francisco Meeting of American Institute of Mining Engineers, Sept. 16-18, 1915.

President Herty appointed Dr. Raymond F. Bacon as representative of American Chemical Society to coöperate with committee of Institute of Chemical Engineering, in the supervision of the Chemical Engineering Catalog, now in progress.

NAVAL ADVISORY BOARD APPOINTMENT.

July 26, 1915.

THE COUNCIL OF THE AMERICAN CHEMICAL SOCIETY.

Gentlemen:

By direction of President Herty, I am writing to each one of you, asking you to nominate two members of our Society to serve on the Naval Advisory Board, of which Mr. Thomas A. Edison is to be Chairman. You have all seen in the public press the announcement of the formation of this Board by Secretary Daniels, and you will accordingly understand its purposes and functions. Briefly, it is a Board to advise the Secretary of the Navy in regard to new inventions and possible methods of improving the defensive and offensive qualities of the American Navy. The following is an extract from Secretary Daniels' letter:

"Will you not, as President of the American Chemical Society, arrange to secure the selection of two of its members to serve on this Advisory Board? I feel that the work your society has done has been such as to give it the right to be, in a way, officially represented, and the Navy Department desires in this way to testify to its own appreciation of the splendid work for our country that your society has done. In addition, I feel that the judgment of your members as to who is best qualified among you to serve on this Board will be far better than my own.

"I am going to ask you, by a poll by letter of your members, or in whatever way seems to you most certain of securing the men desired by the majority of your organization, to choose two of your members to serve on this Board, and it will give me great pleasure, when you have furnished these names, to extend the gentlemen the formal invitation of the Department."

Please place two nominations on a slip of paper and place it in the inclosed ballot envelope. Your name must be written on the outer envelope to identify the nomination, but it must not appear either on or in the ballot envelope.

Should there be no majority vote for any individual, as required by the Constitution, unless objection is made, President Herty will appoint two of the nominees to the Board.

Please give this matter your prompt attention,

Very truly yours,

CHARLES L. PARSONS, *Secretary*.

On August 16, 1915, the ballot was counted by a Committee consisting of F. K. Cameron, R. E. O. Davis and Charles L. Parsons, and report was made to President Herty. Accordingly, he has sent the names of W. R. Whitney and L. H. Baekeland to Secretary Daniels.

MEMBERS ELECTED BETWEEN JULY 15 AND AUGUST 15, 1915.

Ashton, Fred W., College of Agr., Los Banos, P. I.
 Baker, Donald M., 317 Main St., Springfield, Mass.
 Barrett, Wm. F., 42d St. Bldg., New York City.
 Bartlett, Wm. J., 3820 Jackson Blvd., Chicago, Ill.
 Bonsall, Geo. O., 673 St. Hypolite St., Baton Rouge, La.
 Cunliffe, Russell W., 163 Martin St., Milwaukee, Wisc.
 Gorman, George F., Court Ave. & 13th St., S. W., Canton, O.
 Gruber, Rudolf E., 114 Fenway, Boston, Mass.
 Harris, John P., Emporium, Pa.
 Hulings, H. C., Leonia, N. J.
 Magnusson, Carl E., 4521 19th Ave., N. E., Seattle, Wash.
 Nelson, David L., 132 Cattell St., Easton, Pa.
 Pershall, E. E., Kettle River Co., Madison, Ill.
 Polack, Wifrid G., Castner Kellner Alkali Co., Runcorn, Eng.
 Rouaix, Pastor, Vera Cruz, Mexico.
 Smith, Victor J., 6107 Carnegie Ave., Cleveland, O.
 Southwell, Ray, Wichita Flour Mills Co., Wichita, Kans.
 Strubin, Paul, 1215 W. Allegheny Ave., Philadelphia, Pa.
 Theriault, Emery J., U. S. Public Health Service, Cincinnati, O.
 Trigg, Charles W., 359 Meyran Ave., Pittsburgh, Pa.
 Vesely, Frank A., 180 Boston Ave., Tufts College, Mass.
 Wentsler, E. G., 506 Mulberry St., Scottdale, Pa.
 Westman, Leroy E., 317 Queen St., Ottawa, Canada.

DECEASED.

Gail Mersereau, 414 3rd Ave., Brooklyn, N. Y., July 14, 1915.
 John M. Davison, The Upham, Santa Barbara, Calif., July, 1915.
 T. B. Stillman, Fairmount Hotel, Jersey City, N. J., Aug. 10, 1915.

Proceedings.

GENERAL MEETING.

The Fifty-first Meeting of the American Chemical Society was held in Seattle, Washington, August 30 to September 3, 1915, inclusive. The members came to Seattle from many directions although a special car brought thirty-three over the Great Northern railroad on the evening of the 30th. Those who came in the special car spent August 29th in Glacier National Park. The Meeting was opened by an address of welcome by the Dean of the University of Washington to which response was made by President Herty. A general meeting was then called to order and listened to an address by Leo. H. Baekeland on "Chemical Industry" and a second address by H. K. Benson on "Industrial Resources and Opportunities of the Pacific Northwest." Following these addresses the Society continued in general session until noon of the following day holding public symposiums for which the following papers were presented:

Part I. Continuation of series of papers first presented at New Orleans on the Chemist's Contributions to Industry as follows:

"The Contributions of the Chemist to the Naval Stores Industry," by John E. Teeple.

"Contributions of the Chemist to the Iron and Steel Industry," by George W. Sargent.

"Contributions of the Chemist to the Iron and Steel Industry," by A. S. Cushman.

"Contributions of the Chemist to the Art of Soap Making," by M. H. Ittner.

"Contributions of the Chemist to the Perfumery Industry," by R. T. Beiser.

"Contributions of the Chemist to the Lead Industry," by G. W. Thompson.

"Contributions of the Chemist to the Paint and Varnish Industry," by Maximilian Toch.

"Contributions of the Chemist to the Photographic Industry," by Francis C. Frary.

"Contributions of the Chemist to the Pharmaceutical Products Industry," by Frank R. Eldred.

"Contributions of the Chemist to the Hardwood Distillation Industry," by S. W. Katzenstein.

"Contributions of the Chemist to the Packing House Products Industry," by Arthur Lowenstein.

"Contributions of the Chemist to the Electrochemical Industry," by W. S. Landis.

Part II. Symposium on the Chemistry of Wood Distillation.

"Chemical Engineering of the Hardwood Distillation Industry," by James R. Withrow.

"What Chemistry Has Done to Aid the Utilization of Wood," by S. F. Acree.

"The Study of the Tannin Content of Douglas Fir and Western Spruce Sawmill Waste," by H. K. Benson and Thomas G. Thompson.

"Yield of By-Products from the Destructive Distillation of Some Western Conifers," by H. K. Benson and Marc Darrin.

"The Extraction of Resinous Wood by Ammonia," by H. K. Benson and Newton Crites.

"Discoloration of Maple in the Kiln," by Roy C. Judd.

"Waste Pine Wood Utilization," by John E. Teeple.

"The Chemical Composition of the Light Oil from the Destructive Distillation of Resinous Woods," by R. E. Rose and A. G. Bissell.

"Manufacture of Ethyl Alcohol from Wood Waste. II. The Hydrolysis of White Spruce," by F. W. Kressmann.

"The Application of the Davis Spot Test in the Preliminary Examination of Creosotes," by Homer Cloukey.

"Isoprene from Beta-pinene," by A. W. Schorger and Ralph Sayre.

"The Distillation of Douglas Fir at High Temperatures," by Bailey Tremper.

"The Manufacture of Ethyl Alcohol from Wood Waste. III. Western Larch as a Possible Raw Material," by F. W. Kressmann.

"The Production of Acetone from Pyroligneous Acid," by Marc Darrin.

Additional papers read in general session:

"The Relation of Water Power to Chemical Industry," by Henry J. Pierce.

"The Seattle Water Supply," by John Weinzirl.

"The Composition and Properties of Activated Sludge," by Edward Bartow and W. D. Hatfield.

On Wednesday afternoon the various additional programs were held as well as the election of additional officers for 1916. Titles of papers presented to Divisions are printed in the October issue of the *Journal of Industrial and Engineering Chemistry*. On the evening of the 31st, a complimentary Smoker was given by the Seattle Commercial Club, at which Prof. Meany gave a beautifully illustrated lecture with colored slides on Mt. Ranier. The members were also entertained by a Japanese sword contest and by a Chinese cartoonist. Besides the usual attractions of the excursions and the President's address, the ladies were given special entertainment of a reception and tea on the University Campus Tuesday, August 31st, and an organ recital the same evening. On Wednesday they were given a special drive by automobile through the parks and

boulevards of Seattle. On Wednesday the members were treated to an automobile trip through the beautiful parks and boulevards of Seattle and on Wednesday evening at 8 P.M., President Charles H. Herty gave his presidential address entitled "Coöperation in Matters Chemical," before a large audience. On Thursday a complimentary excursion was made on a specially chartered steamer on Puget Sound and refreshments were served to members and guests present. Thursday evening a subscription banquet closed the regular meeting of the Society, although other excursions were enjoyed on Friday. On Friday, September 3rd, a portion of the members were taken by private yachts on Puget Sound to Tacoma and visited plants there, while a party of twenty-nine took automobiles from Tacoma to Mt. Rainier National Park, over one of the most beautiful drives in America. Saturday spent in Portland as the guests of the Oregon Section. The members were met at the train at 8 A.M. and were taken direct to one of Portland's hotels where a complimentary breakfast was served. By automobile the members then visited either the new Gas Plant of the city or the Willamette Paper Company Works at Oregon City. Following these visits, the members met for a complimentary luncheon at Portland's most beautiful Country Club. After lunch the members were shown around Portland by automobile and met at 4 o'clock to listen to a lecture by Messrs. Burger and Jones, illustrated by colored photography lantern slides showing scenes along the Columbia River and views of Mt. Hood and Mt. St. Helens. This set of views is probably the most remarkable and beautiful chemical reproductions of nature that have ever been shown before an audience. The day was thoroughly enjoyed by members present. On September 5th, twenty-five members who had come through together to San Francisco were entertained at dinner at Techau Tavern by the members of the California Section in the usual hospitable manner so characteristic of California chemists. The registration at Seattle showed the presence of 106 members of the Society and 119 guests.

Meetings of the Divisions were held as follows:

Division of Agricultural and Food Chemistry.

In the absence of the chairman and vice-chairman, Charles E. Coates was appointed acting chairman by President Herty. The division held its meeting jointly with the Division of Pharmaceutical and Biological Chemistry. Election of officers for the coming year resulted as follows: L. M. Tolman, *Chairman*; W. D. Bryan, *Vice-Chairman*; George B. Taylor, *Secretary*; A. V. H. Mory, H. A. Huston, E. R. Smith, *Executive Committee*.

CHARLES E. COATES, *Acting Chairman*.

Division of Biological Chemistry.

The Pharmaceutical, the Agricultural and Food Chemistry, and the Biological Chemistry Divisions held a joint session for the reading and

discussion of papers. At the close of the joint session, the Biological Chemistry Division held its annual meeting. A motion to omit the election of new officers was duly made and passed. After a discussion of several topics of interest to the work of the division, the meeting adjourned. The vote of the division as stated above leaves the present officers in power for another year by the by-laws of the division. They are as follows: Carl L. Alsberg, *Chairman*; I. K. Phelps, *Vice-Chairman and Secretary*. *Executive Committee*: W. D. Bancroft, *Chairman*; Edward Kremers, D. D. Van Slyke, A. W. Dox, A. D. Emmett.

ISAAC KING PHELPS, *Secretary*.

Division of Physical and Inorganic Chemistry.

The Division of Physical and Inorganic Chemistry met in Room 204, Bagley Hall at 1.30 P.M., September 1st. In the absence of the chairman and of the secretary, E. C. Franklin and S. J. Bates were appointed chairman and secretary *pro tem*, respectively. Upon the suggestion of the Nomination Committee, the following officers were elected for the coming year: E. W. Washburn, *Chairman*; I. Langmuir, *Vice-Chairman*; James Kendall, *Secretary*; *Executive Committee*: A. W. Brown, W. E. Henderson, A. B. Lamb, F. K. Cameron, H. P. Cady.

STUART J. BATES, *Secretary pro tem*.

Organic Division.

On account of the absence of the regular officers of the division, President Herty appointed Dr. W. J. Hale as acting chairman and Dr. H. L. Fisher as acting secretary. The following officers were elected for the ensuing year: C. G. Derick, *Chairman*; H. L. Fisher, *Vice-Chairman and Secretary*; *Executive Committee*: F. B. Allan, W. J. Hale, E. E. Reid.

H. L. FISHER, *Acting Secretary*.

Division of Industrial Chemists and Chemical Engineers.

The papers read before the division were presented in the general meeting as already outlined. The meeting appointed a committee to present nominations for officers for the ensuing year. The following were duly elected: H. E. Howe, *Chairman*; R. F. Bacon, *Vice-Chairman*; S. H. Salisbury, Jr., *Secretary*; *Executive Committee*: M. C. Whitaker, W. F. Hillebrand, C. H. Herty, H. K. Benson, J. R. Withrow, S. W. Parr.

Division of Pharmaceutical Chemistry.

The division held a joint meeting with Divisions of Biological and of Agricultural and Food Chemistry for the reading of papers. The following officers were elected for the ensuing year: J. H. Long, *Chairman*; H. V. Arny, *Vice-Chairman*; Geo. D. Beal, *Secretary*; *Executive Committee*: F. R. Eldred, C. W. Johnson.

F. R. ELDRDRED, *Chairman*.

The above has been duly entered on the minutes of the Society.

CHARLES L. PARSONS, *Secretary*.

COUNCIL MEETINGS.

The meeting of the Council of the American Chemical Society was held in the Hotel Frye, Seattle, Monday evening, August 30th at 9 P.M., President C. H. Herty in the chair.

The following Councilors were present: A. S. Wheeler, A. D. Thorburn, Edward Bartow, Frank R. Eldred, F. C. Atkinson (substitute for Wm. M. Blanchard), W. A. Noyes, Geo. B. Frankforter, Wm. J. Hale (substitute for S. L. Bigelow), E. C. Franklin, O. F. Stafford, James R. Withrow (substitute for W. E. Henderson), H. K. Benson, T. J. Bryan (substitute for D. K. French), Charles E. Coates, W. D. Richardson, J. H. Long, L. H. Duschak and C. L. Parsons.

A petition was presented from the chemists located at Ames, Iowa, asking for formation of a local section at Ames. A mass of correspondence on the subject was referred to a committee consisting of J. R. Withrow, W. A. Noyes, and F. R. Eldred for recommendation to the Council.

A communication was presented to the Council from E. J. Crane, editor of Chemical Abstracts, setting forth the necessity of printing a ten years' index to Chemical Abstracts. The Council voted that the Secretary in consultation with Mr. Crane should send a subscription blank to all members of the Society this fall, together with a request for support for the publication of this index in order that the Directors might determine whether or not publication is feasible. It was also suggested that Mr. Crane bring this matter before the local sections of the Society in order that the necessity for such an index might be more generally understood.

The committee consisting of J. H. Long, F. R. Eldred, L. F. Kebler, J. M. Francis and B. L. Murray, appointed at New Orleans to consider the position which the Society should take in regard to uniform anti-narcotic laws, presented the following report which was unanimously adopted:

Report of Committee on Uniform Antinarcotic Laws.

WHEREAS, drafts of proposed uniform antinarcotic laws to be enacted by the several states have been suggested by different organizations and committees, notably by the United States Chamber of Commerce and by the National Association of Retail Druggists, and

WHEREAS, the proposed laws are alike in principle but differ somewhat in details as to definitions and suggestions for enforcement,

It is moved as the sense of this Council that while we, as representing the American Chemical Society, do not deem it expedient to adopt in its entirety any one of the proposed drafts we desire to go on record as cordially endorsing the plan of having uniform antinarcotic laws passed by the several states which shall be in harmony with the national laws on the subject as finally construed by the United States Courts.

It is further recommended that for the sake of greater definiteness in

definition and to avoid inevitable confusion the words *synthetic substitutes*, wherever occurring in certain of the proposed drafts, be omitted, and that the same term where used in the national or so-called Harrison Act be eliminated by proper amendment of the Sections containing it.

It is moved that this resolution be given publicity through the Journal and by publication in *Science*.

It was voted that President Herty should appoint a temporary chairman and officer from any Division scheduled to hold meetings at Seattle, that were not represented by their regular officers or substitutes at the meeting. The President appointed Charles E. Coates, chairman of the Division of Agricultural and Food Chemistry; William J. Hale, chairman of the Division of Organic Chemistry; and Dr. Herty, himself, acted as chairman of the Division of Industrial Chemists and Chemical Engineers.

W. A. Noyes was re-elected editor of the *Journal of the American Chemical Society* for 1916 and the old board of associate editors were re-elected with the addition of Dr. John Johnston. E. J. Crane was re-elected editor of *Chemical Abstracts*. M. C. Whitaker was re-elected editor of the *Journal of Industrial and Engineering Chemistry* and the same board of associate editors was re-elected with the addition of Dr. S. F. Acree. The appointment of Dr. Raymond F. Bacon, representing the American Chemical Society, in coöperation with a committee from the Institute of Chemical Engineers, for the supervision of a chemical engineering catalog, was confirmed.

The following resolutions, presented by the Division of Pharmaceutical Chemistry, concerning the so-called "variation clause" of the Federal Food and Drugs Act, were unanimously adopted by the Council:

WHEREAS, it is being proposed to repeal the so-called "variation clause" of the Federal Food and Drugs Act of June 30, 1906, and of similar clauses in State Food and Drug Enactments, thereby making the United States Pharmacopoeia and National Formulary the sole and only standards for all products in every case in which a title recognized in the United States Pharmacopoeia and National Formulary is used, and

WHEREAS, the United States Pharmacopoeia and National Formulary comprise only standards that are limited and are properly applicable only to drug and chemical products which have been specially prepared for use in pharmacy and medicine, and hence are not satisfactory and sufficient as standards for many non-medical and non-pharmaceutical purposes, such as the many uses in the industries and arts, and

WHEREAS, the insistence upon one invariable standard which might not, under any circumstances, be departed from, requires the unwarranted assumption that such standards are incapable of further improvement and would interfere with a proper freedom of choice by physicians in the selection of medicaments and likewise with the freedom of pharmacists

and chemists in the development and introduction of new and superior therapeutic products, therefore,

It is the sense of the members of the Division of Pharmaceutical Chemistry of the American Chemical Society that the variation clause is a necessary and proper part of all Federal and State Food and Drug Laws, and that the repeal of said clause would result in great and unnecessary injury to the legitimate interest of pharmacy, medicine, and industries and arts employing chemicals.

The invitation of the University of Illinois to hold the Spring Meeting of 1916 in Urbana during Easter week was unanimously accepted. The Council voted that time and place of the Fall Meeting for 1916 be left to the President and Secretary with the understanding that as soon as the constitutional limit of one year previous to the date of the meeting had been reached, the President and Secretary would announce New York as the place of the meeting as per previous understanding that the meeting should be held in affiliation with the American Association for the Advancement of Science.

A communication from Dr. H. V. Arny, chairman of the Committee on Weights and Measures of the American Pharmaceutical Association, requesting the cooperation of a committee from the American Chemical Society in behalf of a united campaign of education toward the ultimate adoption and use of the metric system of weights and measures in this country, was presented to the Council. The Council voted that the President should appoint a committee of five to cooperate with the committee of the American Pharmaceutical Association. The committee appointed will be announced in the next issue of the Proceedings.

The question of the appointment of a committee to cooperate with the United States Government to obtain the regular collation and publication of complete and uniform statistics in regard to foreign commerce in chemicals was discussed. The Council voted that the President should appoint a committee of five for this purpose with the request that they call to their aid the editor of the *Journal of Industrial and Engineering Chemistry*, the editor of the *Journal of Commerce*, the editor of the *Oil, Paint and Drug Reporter* and the editor of *Metallurgical and Chemical Engineering*, and that the committee should request each local section to appoint a local member to cooperate with them in the attempt to obtain a detailed and accurate knowledge of chemical imports. The Council voted to refer to the Directors of the Society the allotment of a sum of money not to exceed \$250.00 for the purpose of the committee. The President appointed the following: B. C. Hesse, *Chairman*, A. D. Little, Wm. Hoskins, B. L. Murray and Russell W. Moore.

The following communication from the St. Louis Section of the American

Chemical Society was then presented to the Council, Mr. Lewis B. Allyn having been duly informed of the charges:

"To the Council of the American Chemical Society:

"GENTLEMEN:

"WHEREAS, Lewis B. Allyn, of Westfield, Mass., a member of the American Chemical Society, has written articles tending to throw much suspicion on the prepared foods and beverages sold in this country, to arouse unnecessary alarm among the uninformed public, and especially to influence the purchase of foods, beverages and other preparations advertised in certain publications, and

"WHEREAS, said party is guilty of having made statements that can be explained only on the assumption that he is ignorant or that they are deliberately false, and

"WHEREAS, some of these statements are a libel on the Referee Board of Consulting Scientific Experts, on many food and drug officials, on many manufacturers and chemists employed by them, many of these chemists being members of our Society, and

"WHEREAS, such articles as are herewith exhibited create the impression that the Food and Drug Laws of the States and Federal Government are inadequate, and

"WHEREAS, such articles, to say the least, are most unethical, therefore, be it

"Resolved, that the members of the St. Louis Section of the American Chemical Society respectfully request, unanimously, that Lewis B. Allyn be expelled from the Society, and be it further

"Resolved, that a copy of these resolutions be sent to the President of the Society, Mr. A. D. Little, Chairman of the Committee on Ethics, and the Secretary of each local section."

"Yours very respectfully,

"(Signed) GEO. LANG, JR., Secy. St. Louis Section."

After an extended discussion the following motion was passed:

WHEREAS, the St. Louis Section of the American Chemical Society has adopted resolutions, copy of which is attached hereto, favoring the expulsion of Lewis B. Allyn of Westfield, Mass., from the Society, and

WHEREAS, Mr. Allyn's activities and writings appear to be a part of a larger movement commonly known as the "Westfield Campaign,"

Now, therefore, Be it Resolved, That a committee of five members of the Society be appointed by the President to investigate the so-called "Westfield Campaign," and Lewis B. Allyn's connection therewith, in relation to the subject matter of the resolutions submitted, and that Mr. Allyn and other interested persons be given full opportunity to be heard by the committee, and that the committee report its recommendations at the next General Meeting of the Society.

The President appointed the following committee: M. T. Bogert, J. Stieglitz, W. D. Bigelow, H. C. Lythgoe and E. H. S. Bailey.

The Council then adjourned to meet Thursday morning.

A Council meeting was called September 2nd at 11 A.M. on board the excursion steamer on Puget Sound. The following Councilors were present: C. H. Herty, James R. Withrow (subs.), O. F. Stafford, Charles E. Coates, Geo. B. Frankforter, W. D. Richardson, W. A. Noyes, H. K. Benson, E. C. Franklin, Edward Bartow, L. H. Duschak (subs.), T. J. Bryan (subs.), Frank R. Eldred, Wm. J. Hale (subs.), J. S. Jones, F. C. Atkinson (subs.), O. L. Barneby (substitute for J. H. Walton, Jr.), I. K. Phelps, vice C. L. Alsberg, and C. L. Parsons.

The committee appointed to consider the formation of a local section at Ames, Iowa, reported favorably, and the President and Secretary were directed to give a charter to the Ames members of the Society as soon as a petition was presented in legal form.

President Herty presented to the Council the matters brought up in the presidential address regarding the necessary legislation required for the development of chemical industry in America. A committee consisting of Dr. W. A. Noyes, E. C. Franklin, W. D. Richardson, and C. H. Herty was appointed to consider resolutions in regard thereto and report at an adjourned meeting at 4 P.M.

President Herty presented a letter from Mr. Arthur D. Little, chairman of the committee on "The Adoption of a Code of Professional Ethics." As a result of the discussion, it was voted that the President appoint a new committee of five, Mr. Arthur D. Little as chairman, and that the committee be requested to report at the next General Meeting of the Society. The committee will be announced later. The Council then adjourned to 4 P.M.

On reassembling in the afternoon, the committee appointed to consider the recommendations in the President's address presented a letter which they suggested should be sent by the President of the Society to the President of the United States. After discussion it was voted and it was the unanimous sentiment of the Council meeting held in Seattle that the following letter should be sent by President Herty of the American Chemical Society to President Wilson.

"September 25, 1915.

"The President:

"SIR:

"The following letter has been written at the request of the Council of the American Chemical Society, and has received the unanimous approval of that Body:

"During the recent meeting of the American Chemical Society, at Seattle, the present situation with regard to the manufacture of dyes and other

chemicals in the United States has been under discussion. It is well known that we have been dependent on Germany for many of our most imported dyes, and that some of the textile industries using these have found themselves in a very difficult position since the outbreak of war in Europe.

"We have both the raw materials and the trained chemists essential for the manufacture of these products, but it has been found difficult to secure capital to establish the plants necessary for the supply of our needs. It need hardly be said that it is important to seize the present favorable opportunity to develop this industry in America, if possible.

"A study of the causes which at present interfere with manufactures of this class has led us to the conclusion that one of the most important is the fear that at the close of the war the new industry might be quickly destroyed by the unfair competition which arises from the sale of a foreign product at a price below that at which the same product is sold in its home market. This method of destroying a dangerous competitor has been too common in the past, and is now forbidden by law in the United States. It would seem to be possible to enact laws which will protect our manufacturers from similar practices of foreign corporations.

"It may be that some changes in our tariffs are desirable in the interest of the manufacture of dyes and other chemicals. The Council of the American Chemical Society will not venture an opinion on this point, but would suggest that this is a question which should be carefully considered by disinterested experts who are competent to examine the facts on which an authoritative opinion can be based.

"The industry to which I refer is of such importance to the industrial welfare of our country, that I would most respectfully request that in your next Annual Message you should urge upon Congress the need of legislation designed to eliminate unfair competition from foreign manufacturers. I also earnestly hope that through Congress, or otherwise, information may be secured from disinterested experts as to whether the provisions of our tariff, which relate to the manufacture of dyes, are suitable or not.

"I am sending you herewith copies of a report of a committee of the New York Section of our Society, and of my own recent address as President of the American Chemical Society, in both of which the question of the development of the manufacture of dyes in the United States is considered in more detail.

"I have the honor to be

"Very respectfully yours,

"(Signed) CHARLES H. HERTY, *President.*"

The following resolutions presented by G. B. Frankforter were unanimously adopted: "WHEREAS, in the untimely death of our esteemed

colleague, John Ulric Nef, the American Chemical Society has lost one of its most distinguished members. Be it *Resolved*,—that we the members of the American Chemical Society herein express our deep sorrow at the loss which the Society and the chemical world has sustained. Dr. Nef has ever been known to us as a zealous and untiring worker in the search for the truth, and his life has been to us an inspiration for higher and nobler motives in the realm of science. Be it further *Resolved* that a copy of these resolutions be sent to his son John and at the same time spread upon the minutes of the Society."

The Council voted unanimously the thanks of the American Chemical Society to H. G. Byers, H. K. Benson, E. J. Bartells, Lee A. White, J. H. Linton, C. A. Newhall, M. K. Falkenburg and Mrs. C. A. Newhall, chairmen of the local committees for the Seattle Meeting and their vote of thanks to the members of their committees for their untiring care of the members at Seattle and for their work toward a successful meeting of the Society at Seattle. Also thanks to Mr. Louis Heinrich of the Seattle Brewing & Malting Company for the courtesies extended to the visiting delegates by him; to the Commercial Club; to the faculty of the College of Science, and to the faculty of the Ladies' Club for the entertainment provided by them for the members of the Society.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

COUNCIL.

MEMBERS ELECTED BETWEEN AUGUST 15 AND SEPTEMBER 15

Boehmer, Harold R., 340 Sheridan Ave., Whiting, Ind.
 Civis, James A., 114 4th St., Sturgis, Mich.
 Crow, Elmer Z., American Trust & Savings Bank, Birmingham, Ala.
 De Grote, Melvin, 241 Mass. Ave., Detroit, Mich.
 Easterbrooks, Frank D., 43 Dove St., Albany, N. Y.
 Hart, De Loss G., 618 No. O St., Tacoma, Wash.
 House, Harry H., 1053 Chestnut St., Riverside, Calif.
 Hudgins, L. A., Y. M. C. A., Dallas, Tex.
 Humphries, H. B. P., Schenley Hotel, Pittsburgh, Pa.
 Jones, W. B., 179 Kearny Ave., Perth Amboy, N. J.
 Miller, George A., Jr., Box 37, Auburn, Ala.
 Morrison, D. R., Bowmanville, Ontario, Canada.
 Nicolet, A. C., 3741 Warwick Blvd., Kansas City, Mo.
 Peterson, Geo. O., 357 S. Homan Ave., Chicago, Ill.
 Schwerlfeger, Hans, 6216 Corson Ave., Seattle, Wash.
 Senior, George, Y. M. C. A., Newton, Mass.
 Smith, Roscoe B., Pike, N. H.
 Thornton, Harrison R., 10 Laurel Ave., Auburn, Me.
 Wakefield, J. M., Cerro de Pasco Mining Co., La Fundicion, Peru.
 Weitz, Augustine H., Mayburg, Pa.
 Whipple, A. Floyd, Foster House, Sheridan Road, Evanston, Ill.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 50, Washington, D. C.]

SOUTHERN CALIFORNIA SECTION.

The midsummer meeting of the Section was held August 18th in conjunction with the American Institute of Chemical Engineers. The papers of the evening were, "A New Electrical Method of Sewage Disposal," by Dr. John C. Olsen, and "Fleming Dust Collecting System," by W. C. Hanna.

H. L. PATHE, *Secretary*.

PITTSBURGH SECTION.

The 119th regular meeting was held September 16th. The papers of the evening were, "Some Aspects of the Optical Glass Industry; Present Condition of the Industry, and Some of the Manufacturing Problems," by C. C. Rand; "Trivalent Manganese in Glass," by S. R. Scholes; "The Determination of the Critical Constants and Vapor Pressures at Moderately High Temperatures," by G. A. Burrell.

W. C. CORN, *Secretary*.

CHICAGO SECTION.

The regular September meeting was held September 17th. The feature of the evening was a moving picture and explanatory lecture on "The Evolution of Zion Laces and Lace Curtains from the Cotton in the Field to the Finished Product," by C. D. Heller, advertising manager, Marshall Field & Co.

D. K. FRANCE, *Secretary*.

DETROIT SECTION.

The first regular meeting of the season 1915-1916 was held September 16th. The paper of the evening was, "Disinfection of Public Water Supplies," by C. A. Jennings, of Chicago.

EDW. J. GUTACNA, *Secretary*.

DECEASED.

J. S. Wm. Greth, 221 1st Ave., Pittsburgh, Pa., August 7, 1915.

J. U. Nef, University of Chicago, Chicago, Ill., August 13, 1915.

James G. Woolworth, 220 Waterman St., Providence, R. I., Sept., 1915.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND OCTOBER 15, 1915.

Anderson, R. J., N. Y. Experiment Station, Geneva, N. Y.
Arnstein, Henry, 23rd and Minnesota Sts., San Francisco, Calif.
Auleb, Chauncey, 124 So. 8th St., Newark, N. J.
Brallier, P. S., Box 261, State College, Pa.
Brauer, O. L., 2115 Merced St., Selma, Calif.
Byron, Oscar, 550 Washington Ave., Carnegie, Pa.
Carter, Gardner L., Box 65, University, Va.
Choudhari, Tarini Charan, Ghoramara, Rajshahi, India.
Clifford, Charles W., 1015 University Ave., Madison, Wis.
Curry, James S., 225 West 120th St., New York City.
Dickerson, Loren B., 155 Perry St., New York City.
Dickson, Ross H., 86 St. James Ave., Boston, Mass.
Edmunds, Arthur D., Norwich University, Northfield, Vt.
Ellithorp, John Stafford, Jr., 426 Ostrom Ave., Syracuse, N. Y.
Ensel, Harry R., 151 West 140th St., New York City.
Fehl, Paul B., 725 Walnut St., Reading, Pa.
Foster, Goodwin L., Sharon, Mass.
French, Herbert E., 704 So. Third St., Champaign, Ill.
Friedrich, Edmund, 516 West 135th St., New York City.
Fuller, Everett W., 2 Tennis Court, Brooklyn, N. Y.
Gosserand, Morris A., St. Rose P. O., La.
Green, E. Louis, 4126 Shenandoah Ave., St. Louis, Mo.
Hadfield, Wm. H., 554 Monroe Ave., Elizabeth, N. J.
Hazard, Irving W., Syracuse University, Syracuse, N. Y.
Haylett, Robert E., 2 Roanoke Road, Wellesley, Mass.
Hetchner, Lea S., 246 Van Buren St., Newark, N. J.
Hornbruch, Walter, 891 So. 16th St., Newark, N. J.
Ishikawa, Ichiro, c/o Dr. J. Takamine, Equitable Bldg., N. Y.
Jacobs, Walter A., Rockefeller Institute for Medical Research, 66th St., and Ave. A., New York City.
Jacobson, Simon, 1189 Boston Road, New York City.
Jarvis, Ernest G., Dominion Steel Foundry Co., Hamilton, Ont., Canada.
Jeffreys, Elizabeth, Glasgow, Mo.
Kinter, George R., Section A., Taylor Hall, So. Bethlehem, Pa.
Knowles, Chester L., 411 Brook St., Providence, R. I.
Lamie, Ralph D., 260 Belvidere Ave., Detroit, Mich.
Langdon, S. C., 5018 19th Ave., N. E., Seattle, Wash.
Langendorf, H., Midland, Mich.
Langreck, Frederick Burton, 4177 Flad Ave., St. Louis, Mo.
Lepshye, William J., 959 Westchester Ave., New York City.
Lubarsky, George H., 69 Wall St., New York City.
Nagelvoort, Adriaan, 52 E. 41st St., New York City.
Nenninger, Ross F., 279 Meeker Ave., Newark, N. J.
Olewine, James Harris, 412 E. Daniel St., Champaign, Ill.
Peirce, Joseph Otis, c/o A. P. M. Co., Beaver Falls, Pa.

Plautz, Charles H., 442 Dimmeck St., Watertown, N. Y.
 Putnam, Mark E., Midland, Mich.
 Randolph, Edward, 2350 Broadway, New York City.
 Rice, Wayland Wilbur, 12 Dudley St., Providence, R. I.
 Roberts, R. Chester, 251 So. Forsythe, Franklin, Ind.
 Saunders, R. E., Union Carbide Co., Sault Ste. Marie, Mich.
 Sawens, R. H., 232 Clairmonte Ave., Syracuse, N. Y.
 Scharf, James M., 306 Allen St., State College, Pa.
 Silver, J. Robinson, Jr., Emporium, Pa.
 Sherwood, F. F., University of S. Dak., Vermillion, S. Dak.
 Stewart, Douglas A., 2524 S. Cleveland Ave., Philadelphia, Pa.
 Thomas, Alexander R., 675 Highland Ave., Newark, N. J.
 Thompson, J. V., 1225 Fayette St., N. S., Pittsburgh, Pa.
 Tuttle, J. Ross, Hartley Hall, Columbia University, New York City.
 Valentine, Kenneth S., 550 W. 114th St., New York City.
 Van Valkenburgh, E. A., Box 70, Hartley Hall, Columbia University,
 New York City.

CORPORATION MEMBER.

Goldschmidt Detinning Co., 60 Wall St., New York City.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

RHODE ISLAND SECTION.

At the meeting held September 25th, the following officers were elected to serve for the coming year: *President*, Dr. Augustus H. Fisk; *Vice-President*, Robert K. Lyons; *Secretary-Treasurer*, Dr. Robert F. Chambers; *Member of Executive Committee*, Clarence P. Bearce.

WM. H. CADY, *Secretary pro tem.*

INDIANA SECTION.

The first fall meeting was held October 8th. Mr. F. B. Wade, the retiring president, gave a paper on "Color in Precious Stones." The annual election of officers resulted as follows: *President*, J. H. Ransom; *Vice-President*, H. E. Jordan; *Secretary-Treasurer*, H. W. Rhodhamel; *Executive Committee*, F. B. Wade, W. C. Bartholomew, A. B. Davis.

H. W. RHODAMEL, *Secretary.*

NASHVILLE SECTION.

The 35th meeting was held October 15th. The program included the following address: "The Bureaus of Mines and Standards," by Dr. Paul C. Bowers.

VICTOR P. LEE, *Secretary.*

PITTSBURGH SECTION.

The October meeting was held jointly with the American Electrochemical Society, October 21st. Program: "Electric Furnaces for High Temperature Industrial Chemical Work," by F. T. Snyder, Snyder Electric Furnace Company, Chicago.

W. C. COVE, *Secretary.*

ST. LOUIS SECTION.

Meeting of October 11, 1915. Mr. H. E. Wiedemann gave an illustrated address on "The Industrial Utilization of Peat." Mr. E. J. Sheppard, of the National Lead Co., described an "Apparatus for the Determination of the Degree of Fineness of Paint Pigments."

GEO. LANG, JR., *Secretary.*

OREGON SECTION.

The 23rd regular meeting was held October 2nd. The principal paper of the evening was presented by Mr. J. R. Cornog, on the subject: "The Operation of a Modern Soap Plant."

F. A. OLMSTED, *Secretary.*

CONNECTICUT VALLEY SECTION.

The thirty-fourth meeting was held October 9th. Program: Report on "The New York Exposition of Chemical Industries," by Mr. Hoover. "The American Cotton Industry as seen by the Industrial Chemist," by Dr. Frederick Dannerth.

R. J. MARSH, *Secretary.*

CLEVELAND SECTION.

The Section met Monday evening, October 11th. Mr. William Roy Mott, of the National Carbon Company, addressed the Section on "The Use of the Flaming Arc in Paint and Dye Testing."

A. F. O. GERMANN, *Secretary.*

UNIVERSITY OF MISSOURI SECTION.

The 61st meeting was held September 24th. Dr. P. F. Trowbridge spoke on "Commercial Fertilizers in Missouri—the Method of Legal Control and How the Industry is Affected by Present War Conditions."

HENRY L. DAHM, *Secretary.*

CINCINNATI SECTION.

The 200th regular meeting was held October 13th. Dr. C. P. T. Fennel delivered a talk on "Old Chemical Symbols" (illustrated).

STEPHEN J. HAUBER, *Secretary.*

CALIFORNIA SECTION.

The eighty-fifth regular meeting was held September 25th. The paper of the evening was entitled, "Experiences of a Chemist in the Philippines," by S. A. Weirman, late Chemist in Charge of Explosives in the Philippines for the United States Navy.

BRYANT S. DRAKE, *Secretary.*

NEW YORK SECTION.

A special meeting, inaugurating the session of 1915-1916, was held in conjunction with the National Exposition of Chemical Industries, at the new Grand Central Palace, on Friday, September 24th.

After some introductory remarks, the chairman presented to the meeting Dr. Chas. H. Herty, President of the American Chemical Society, who addressed the meeting, speaking on the present occasion as the first

attempt to hold a national exposition of the chemical industries in this country and the support which the enterprise should receive from the industries.

The following papers were read: L. H. Baekeland, "Chemical Industry;" Howard H. Gross, President Tariff Commission League, "The Tariff Question;" S. P. Sadtler, "Some American Contributions to the Chemical Industries."

The first regular meeting of the session of 1915-16 was held October 8th. Program: I. F. Stone, "The Status of the Chemical Industries in the United States at the End of 1915;" Maximilian Toch, "The Barium Industry in the United States Since the European War."

C. M. JOTCH, *Secretary*.

PUGET SOUND SECTION.

A meeting of the Section was held October 9th. The paper of the evening was by Mr. R. T. MacMichael on "The Physics of the Clay Molecule," a discussion of the theory of the plasticity of clay.

H. L. TRUMBULL, *Secretary*.

CHICAGO SECTION.

The regular meeting was held October 15th. The paper of the evening was by Dr. Edward Bartow, on "The Purification of Sewage by Aeration in the Presence of Activated Sludge."

D. K. FRENCH, *Secretary*.

ROCHESTER SECTION.

The first annual meeting was held October 4th. Dr. Bernhard C. Hesse, Consulting Chemist, New York City, discussed the "Paige Bill."

The regular meeting was held October 18th. Mr. Lincoln Burrows spoke on "Glycerine."

H. H. TOZIER, *Secretary*.

DECEASED.

John K. Hamilton, 1229 Buena Vista St., Pittsburgh, Pa., October, 1915.
H. H. McGregor, Adelbert College, Cleveland, O., September 13, 1915.
Hugh Allan Murta, Carman, Man., Canada, September, 1915.

Proceedings.

COUNCIL.

President Herty has appointed the following members to serve on the Committee on Code of Professional Ethics: A. D. Little, *Chairman*, L. H. Baekeland, W. D. Bancroft, William Brady, and F. K. Cameron.

The Executive Committee of the Division of Physical and Inorganic Chemistry have elected Dr. Irving Langmuir as Chairman of the Division instead of Prof. E. W. Washburn, who declined the Chairmanship on account of great pressure of work.

MEMBERS ELECTED BETWEEN OCTOBER 15 AND NOVEMBER 15, 1915.

- Adams, Eugene Gerald, Norwich University, Northfield, Vt.
Amon, Jesse C., 4447 Sewickley Rd., Bellevue, Allegheny Co., Pa.
Bailey, Nat. A., 428 N. Charter St., Madison, Wisc.
Ball, John M., 113 De Witt Place, Ithaca, N. Y.
Barrows, E. R., 3223 Library Ave., Cleveland, Ohio.
Beckers, Dr. W., Ditmas Ave. & 83rd St., Brooklyn, N. Y.
Bennett, Harry T., 2932 Clinton St., Lincoln, Nebr.
Botkin, C. W., 421 N. Wheaton Ave., Wheaton, Ill.
Brown, J. Lyman, 408 E. Green St., Champaign, Ill.
Brown, Wilbur F., c/o Ball Bros. Glass Mfg. Co., Muncie, Ind.
Butterfield, Alice Dacre, Penna. College for Women, Pittsburgh, Pa.
Caldwell, Thos. B., Wilmington, N. C.
Craig, Archibald G., 48 Tonnele Ave., Jersey City, N. J.
Crawford, Frederick North, 805 West Illinois St., Urbana, Ill.
Davidson, Carl N., 917 W. Green St., Urbana, Ill.
Dodge, Wm. E., 415 W. Highland Ave., Shawnee, Okla.
Gavron, Joseph L., 1010 South St., Philadelphia, Pa.
Goss, Byron C., Graduate College, Princeton, N. J.
Greathouse, Lucien H., Bureau of Soils, Dept. Agriculture, Washington, D. C.
Greenfield, Edman, 610 W. Oregon St., Urbana, Ill.
Gundlach, Emanuel G., 428 Wyoming Ave., Buffalo, N. Y.
Hanke, Milton Theo., 5655 S. Drexel Ave., Chicago, Ill.
Harris, Edgar W., Washington, Miss.
Harrison, Julia Peachy, Sweet Briar College, Sweet Briar, Va.
Haskins, J. D., Zemmer Chemical Co., Pittsburgh, Pa.
Hoojendijk, Gerard van Rossen, Chemistry Laboratory, Univ. of Ill., Urbana, Ill.
Jacoby, Henry E., 95 Liberty St., New York City.
Johnson, Theodore, Obispo 30, P. O. B. 750, Havana, Cuba.
Jameson, Charles F., 57 Lowden Ave., W. Somerville, Mass.
Koebig, Dr. Julius, 1025 Union Oil Bldg., Los Angeles, Calif.
Kreiser, Walter H., 91 Linden Ave., Jersey City, N. J.
Lee, Theophilus Henry, Servico Geologico e Mineralogico do Brazil, Ministerio da Agricultura, Rio de Janeiro, Brazil.
Lynas, W. H., 1318 Oak St., Columbus, Ohio.

Lyons, Robert J., Cottrell Co., Ltd., Walkerville, Ontario, Canada.
 Martin, Frederick H., 52 Jefferson Rd., Princeton, N. J.
 McBride, John F., 550 E. Ritter Ave., Indianapolis, Ind.
 McCormack, Joseph M., 112 East Green St., Champaign, Ill.
 McEllroy, William Schaefer, 115 Maple Ave., Edgewood Park, Pa.
 McKee, Wm. Gerard, 501 Allen St., Syracuse, N. Y.
 Meister, Walter F., 2935 Russell Ave., St. Louis, Mo.
 Millar, Russell W., 504 Daniel St., Champaign, Ill.
 Minnig, H. D., Solvay Club House, Syracuse, N. Y.
 Mooney, Luke, c/o N. J. Glue Company, Perth Amboy, N. J.
 Murrill, Paul I., Copper Hill, Tenn.
 Nelson, Wm. G., 47 East Warren Ave., Detroit, Mich.
 O'Brien, W. J., 1722 Euclid St., N. W., Washington, D. C.
 Oppenheim, Dr. S. R., 815 S. Sycamore, Santa Ana, Calif.
 Pierson, R. H., 603 S. Race St., Univ. of Ill., Urbana, Ill.
 Piguet, Leon A., 415 Center St., Solvay, N. Y.
 Ray, A. B., 103 Highland Pl., Ithaca, N. Y.
 Richardson, Anna E., University of Texas, Austin, Texas.
 Riley, Donald, 1822 Sheridan Rd., Evanston, Ill.
 Robinson, Clark S., 42 Crescent St., Cambridge, Mass.
 Sanborn, Mac H., Guanica Centrale, Ensenada, Porto Rico.
 Sasse, A. R., 105 West 36th St., Kansas City, Mo.
 Shum, N. C., 144 University Station, Urbana, Ill.
 Smith, Irene Fern, 607 Michigan Ave., Urbana, Ill.
 Souther, Miss Nathalie Ben, Listman Mill Co., La Crosse, Wisc.
 Stanwick, Chas. A., 419 Main St., Orange, N. J.
 Takamine, Jokichi, 550 W. 173 St., New York City.
 Thompson, R. S., Highlands, Calif.
 Webber, Arthur H., 16 Thorndike St., Beverly, Mass.
 Winkelmann, Herbert A., 121 Chemistry Bldg., Urbana, Ill.
 Williams, Arthur E., 611 Indiana Ave., Urbana, Ill.
 Wright, Fred E., 2134 Wyoming Ave., N. W., Washington, D. C.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

PITTSBURGH SECTION.

The 120th regular meeting of the Section was held October 21st, as a joint meeting with the American Electrochemical Society.

The Section endorsed a resolution by Prof. F. C. Phillips to consider possible ways and means to preserve from destruction the old Priestly Home at Northumberland, Pa.

F. T. Synder, Chicago, read a paper on "Electric Furnaces for High Temperature Industrial Chemical Work."

W. C. COPE, Secretary.

NORTHEASTERN SECTION.

At the meeting of the Section held October 29th, Professor John E. Bucher, of Brown University, spoke on "Fixation of Atmospheric Nitrogen."

GRINNELL JONES, Secretary.

MINNESOTA SECTION.

The 53rd meeting of the Section was held October 22nd. The following officers were elected for the ensuing year: *President*, F. J. Alway; *Vice-President*, C. F. Sidener; *Treasurer*, F. B. Kingsbury; *Secretary*, Sterling Temple; *Councilor*, W. H. Hunter.

Program: Short talks by E. F. Exnor, Geo. B. Frankforter, C. H. Walter and address by retiring Pres. R. W. Thatcher on "Graduate Work in Chemistry."

STERLING TEMPLE, *Secretary*.

UNIVERSITY OF MISSOURI SECTION.

The 62nd meeting of the Section was held October 22nd. Dr. C. R. Moulton addressed the Section on "Units of Reference for Basic Metabolism."

HENRY L. DAHM, *Secretary*.

NEW YORK SECTION.

The regular meeting was held November 12th. Program: "University and Industry," speakers: Nicholas Murray Butler, President Columbia University; M. C. Whitaker, Professor, Chemical Engineering, Columbia University; W. J. Gies, Professor, Biological Chemistry, Columbia University; Charles E. Lucke, Professor, Mechanical Engineering, Columbia University. Paper (read by title) on, "The Synthesis of Certain Substituted Syringic Acids," by Edward Plaut and M. T. Bogert.

C. M. JOYCE, *Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

The first regular meeting of the season was held October 14th. The paper of the evening was by Drs. C. W. Balke and B. S. Hopkins, on "Determination of the Atomic Weight of Yttrium."

G. D. BERL, *Secretary*.

UNIVERSITY OF MICHIGAN SECTION.

The October meeting of the Section was held October 26th. Dr. C. C. Meloche gave a paper on "The Derivatives of Percevic Oxide."

H. H. WILLARD, *Secretary*.

PHILADELPHIA SECTION.

In lieu of the regular October meeting of the Section a joint meeting with the Franklin Institute was held October 28th. Program: "The Development of a Dynamic Theory of Soil Fertility," illustrated by lantern slides, by Frank K. Cameron, Ph.D., Bureau of Soils, United States Department of Agriculture, Washington, D. C.

In addition to the regular November meeting, a special joint meeting with the Franklin Institute was held November 4th. Program: "The Turpentine Industry in the Southern States," illustrated by lantern slides and various exhibits, by Dr. Charles H. Herty, President of the American Chemical Society.

C. S. BRINTON, *Secretary*.

KANSAS CITY SECTION.

The program of the Section on October 16th was as follows: Papers by Prof. L. E. Sayre, "The Hydrogenation of Oils;" A. W. Estabrook, "Wheat and Flour Testing."

W. B. SMITH, *Secretary*.

NEBRASKA SECTION.

The October meeting of the Section was held October 23rd. The topic for the evening was "Recent Research in the Department of Chemistry at the University of Nebraska." Organic, Prof. Mary L. Fossler; inorganic, Dr. Benton Dales.

H. M. PLUM, *Secy*.

LOUISIANA SECTION.

The 88th meeting was held October 22nd. Program: "Formations in Yellowstone Park," Dr. Philip Asher.

F. W. LEIPNER, *Secy*.

WISCONSIN SECTION.

The October meeting of the Section was held October 20th. The following papers were presented: "Studies in the Measurement of the Conductivity of Electrolytes," Dr. W. A. Taylor; "Examination of Woods," Mr. A. W. Schorger.

A. E. KOENIG, *Secretary*.

CONNECTICUT VALLEY SECTION.

The 35th meeting of the Section was held November 6th. Program: "The Manufacture of Rubber Covered Insulated Wire," Mr. Maxwell M. Kahn; "Need of and Methods of Stimulating Increased Employment of Chemistry in Manufacturing Industries," Mr. R. J. Marsh.

R. J. MARSH, *Secretary*.

NEW HAVEN SECTION.

The regular meeting of the Section was held November 10th. Dr. John P. Street, of the Connecticut Agricultural Experiment Station, addressed the Section on the subject, "Patent Medicines."

GEORGE S. JAMIESON, *Secretary*.

CLEVELAND SECTION.

The November meeting of the Section was held November 8th. Professor C. H. Fulton, head of the Mining Engineering Department of Case School of Applied Science, addressed the Section on "The Flotation Process of Ore Concentration." The following officers were elected to serve for the ensuing year: *President*, W. C. Moore; *Secretary-Treasurer*, A. F. O. Germann; *Councilors*, O. F. Tower, E. C. Holton; *Managers*, H. D. Batchelor, J. H. Herron.

A. F. O. GERMAN, *Secretary*.

ROCHESTER SECTION.

A special meeting was held November 8th. Dr. Charles H. Herty, President of the American Chemical Society, spoke on "National Self Containedness in Chemical Industry."

The regular meeting was held November 15th. Dr. H. T. Clarke spoke on "The Chemistry of Dyes."

H. H. TOBIER, *Secretary*.

OREGON SECTION.

The 24th regular meeting of the Section was held October 30th. Mr. N. F. Titus, of the American Gas Incinerator Company, presented the paper of the evening on the subject "Garbage Disposal."

F. A. OLMESTED, *Secretary*.

MARYLAND SECTION.

The 8th regular meeting of the Section was held November 13th. Program: Geo. L. Ringel, of Fritzsche Bros., New York, "The Distillation of Essential Oils from Antiquity to Modern Days."

FRANK M. BOYLES, *Secretary*.

RHODE ISLAND SECTION.

The November meeting of the Section was held November 11th. The speaker for the evening was Mr. Leonard W. Cronkhite, of Boston, Mass., who addressed the Section on "Some Problems of the Chemical Industry during the Past Year."

ROBERT F. CHAMBERS, *Secretary*.

NASHVILLE SECTION.

The 36th meeting of the Section was held November 19th. Program: "Tashiro's Method of Carbon Dioxide Determination," by Prof. E. E. Reinke, of the Department of Biology of Vanderbilt University.

VICTOR P. LEE, *Secretary*.

INDIANA SECTION.

The Section met November 20th. A very interesting program was given in the following three papers: "Calculation of the Alkalinity of Intestinal Juice," by C. E. May; "Experiments in Antimony and Tin Plating," by F. E. Mathers; "Some Problems in the Amalgamation of Precious Metals," by R. E. Lyons.

H. W. RHODEHAMER, *Secretary*.

MILWAUKEE SECTION.

A meeting of the Section was held October 28th. Prof. Louis Kahlenberg, of the University of Wisconsin, gave a talk on "A Fundamental Principle of Chemistry Which Has Been Much Neglected."

BEN L. SALOMON, *Secretary*.

ST. LOUIS SECTION.

The regular meeting was held November 8th. Program: "Organization and Research Work Being Carried on by the Bureau of Chemistry, U. S. Department of Agriculture," by Dr. Carl L. Alsberg, Chief, Bureau of Chemistry; "The Biological Significance of Creatin and Creatinin," by Dr. A. P. Shafer, Washington University Medical School.

GEO. LANG, JR., *Secretary*.

CINCINNATI SECTION.

The 201st regular meeting was held November 10th. Program: "Some Recent Developments in Nitrogen Filtration," by Dr. A. W. Davison.

STEPHEN J. HAUSER, *Secretary*.

DETROIT SECTION.

The October meeting was held October 21st. Program: "The Solid and Enduring Satisfactions of Life," by Dr. Stanley Coulter.

The November meeting was held November 18th. Program: "Some Practical Applications of Our Knowledge of Immunity," by Dr. Severance Burrage of Eli Lilly & Co.

HOW. J. GUTSCHER, *Secretary*.

CALIFORNIA SECTION.

The eighty-sixth regular meeting was held October 23rd. Program: "Cast Iron as Applied to Chemical Industry," by Edward J. Fowler. The following officers were elected to serve for the ensuing year: *President*, Fred G. Cottrell; *Vice-President*, Joel H. Hildebrand; *Secretary-Treasurer*, Bryant S. Drake; *Councilors*, J. Pearce Mitchell, Abbot A. Hanks.

BRYANT S. DRAKE, *Secretary*.

CHICAGO SECTION.

The regular meeting was held November 12th. Program: "Rubber and Methods of Its Manufacture," by C. E. Bradley, of the Mishawaka Woolen Mfg. Co.

D. K. FRENCH, *Secretary*.

AMES SECTION.

At the first meeting of the Section, the following officers were elected to serve for the ensuing year: *President*, J. A. Wilkinson; *Vice-President*, P. E. Brown; *Secretary-Treasurer*, W. G. Gaessler; *Councilor*, W. F. Coover.

W. G. GAESSLER, *Secretary*.

DECEASED.

Robert L. Maury, 51 Lake St., Saranac Lake, N. Y. Died October, 1915.
N. Frederick Merrill, University of Vermont, Burlington, Vt. Died October 26, 1915.

Edward H. Norton, 180 Meadow St., New Haven, Conn. Died October, 1915.

J. Roemer, White Plains, N. Y. Died October, 1915.

Wirt Tassin, 1423 R St., Washington, D. C. Died November 2, 1915.









UNITED STATES
DEPARTMENT OF JUSTICE
FEDERAL BUREAU OF INVESTIGATION